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Technical Manual for Process Sampling Strategies for Organic Materials

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**TECHNICAL MANUAL
FOR PROCESS SAMPLING STRATEGIES
FOR ORGANIC MATERIALS**

by

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SECTION I

INTRODUCTION

The purpose of this technical manual is to describe the sampling approaches for conducting an environmental assessment survey and control technology studies on the feed, product and waste streams associated with the production of organic materials. The intent is to provide selected "state-of-the-art" sampling techniques that can be employed to obtain samples of materials for both chemical analysis and biological testing. The methods presented can be used by all groups involved in this type of sampling, although modifications may be required for particular sites. These methods are presented as extensions of current art and should be viewed as reasonable approaches that will be subject to refinement as further advances are made.

The following description taken in part from the two guideline documents on environmental assessment sampling and analysis programs defines a portion of our area of interest.^{1,2}

"An environmental source assessment contains (1) a systematic evaluation of the physical, chemical, and biological characteristics of the streams associated with a process; (2) predictions of the probable effects of the streams on the environment; (3) the prioritization of the streams; and (4) identification of any necessary control technology program. An environmental source assessment program addresses, to the

maximum extent possible, the identification of potential problems with pollutants for which specific standards have been set and materials that are suspected to have deleterious effects on the environment. The ultimate goal of an environmental source assessment, then, is to insure that the waste streams from a given process scheme are "environmentally acceptable" or that adequate technology exists for control.

The overall strategy incorporates three "levels" (phases) of information development. In general, the intent of each phase is the measurement of the mass flow rates of primary pollutant classes either out of the envelope containing the process or out of the plant of which the process is one part. The strategy which has been developed includes characterization of feed streams to provide a rough material balance, and to determine if an effective control approach may be through feedstock modification. The characterization also extends to the product streams whenever they may directly affect the environment at the next step of usage.

Level I is structured to produce a cost effective information base for prioritization of streams and for planning of any subsequent programs. It seeks to provide input data to support evaluation of the following questions:

- a. Do streams leaving the process have a finite probability of exceeding existing air, water, or solid waste standards or criteria?
- b. Do any of the streams leaving the process contain any classes of substances that are known or suspected to have adverse environmental effects?
- c. Into what general categories (classes) do these adverse substances fall?

- d. What are the most probable sources of these substances?
- e. Based on the adverse effects and mass output rates, what is the priority ranking of streams?
- f. For streams exhibiting potential environmental effects, what is the basic direction that control strategies are likely to follow?

The Level I measurement program provides information on physical and chemical composition of process streams. It provides information on the *in vitro* cytotoxicity and mutagenicity of the streams and stream components as well. In the chemical analysis program information concerning the elemental composition and the distribution of chemical substances according to conventionally, but broadly, defined classes is sought.

This program provides data that permit both the identification of existing broad problems and the evaluation of the possible adverse environmental effects of the streams. The measurement techniques employed in Level I do not attempt the quantitative determination of compliance with existing standards, but instead provide results that can be used both for semiquantitative evaluation of process compliance and for planning subsequent sampling and analysis programs.

Such subsequent programs are effected through Level II and Level III sampling and analytical studies. Briefly, the Level II measurement program is an extensive qualitative, semiquantitative approach that seeks to identify specific substances that exist in any streams having a significant environmental problem. At the conclusion of Level II, the physical, chemical, and biological characteristics of the

stream should be well understood in a qualitative, semiquantitative sense under the normal operating conditions of the process. Level III is a quantitative study of the effect of process variables on the emission rates of specific substances that have been identified in Level II as appropriate "indicators" of the environmental impact of streams. Both Level II and Level III provide the information necessary for the development of control technology - an area of equal importance to the emission assessment of the source.

It is desirable to provide measurement methods that will insure comparability of information from a wide range of processes. At Levels II and III, much of the work will be very process- and stream-specific. Present indications are that a reasonably specific set of procedures can be defined for Level I studies."

Based on these definitions, the current state of the sampling art would usually provide sufficient samples for the sensitivity of the available analytical techniques. However, the additional requirement to provide samples not only for chemical analysis but also for biological effect studies indicates that a larger quantity of samples (approximately 500 mg) is necessary. For health studies, fractionation of particulate matter in size ranges of 3 to 10 μm and less than 3 μm (based on the inhalable size ranges of particulates) is desirable and sufficient samples should be collected in each size range for chemical analysis and toxic effect evaluation. However, the collection of these samples in a short time period implies that assessment programs will involve sampling with higher volume equipment (mass flow) than the currently popular 1 cfm commercial sampling trains.

This manual presents approaches that can be used by persons who are basically knowledgeable in sampling. This means that experience in the techniques is required.

There will, of course, be occasions in which changes in design and operating conditions may be indicated and in such situations experience will be helpful. The methods presented are advances in the "state-of-the-art", not the ultimate solution to all situations. These techniques provide a high probability of success if used with understanding and responsibility.

In an organic sampling effort, problems can be anticipated due to the labile nature of the compounds. Vapor pressure effects can be very serious, and as a result, pressure and temperature control of the sampling system must be considered carefully. Many organic process streams will contain a wide range of chemical compounds, and any one stream may contain all three physical states; solids, liquids, and gaseous. Organic process reactions seldom give 100% yield of the desired product, and the many side reactions that occur can produce a wide range of chemical compounds.

The adsorption of organic compounds on inorganic substances is very common, and adsorption-desorption processes can occur within the sampling system. Reactions can occur during sampling, and as a result, the compounds that are subsequently identified in analysis may not be the compounds actually present in the original process stream.

For the most part, moisture sensitive materials will not be found in exhaust stacks from processes as the materials will react before they can be sampled. However, if the actual process streams are sampled, sufficient moisture may not be

present and, if these are to be collected unchanged, precautions must be taken.

As for example, anhydrides and acid chlorides would form acids upon hydrolysis. In sampling these materials, it is essential that moisture laden air be excluded from the apparatus.

Compounds such as aldehydes can undergo air oxidization to the corresponding alcohol. Formaldehyde is difficult to sample due to polymer formation and the fact that such low molecular weight species may not be collected in total in the adsorber approach.

Examples of unstable compounds are peroxides, dienes, and some polycyclic aromatic compounds. Peroxides can decompose spontaneously and under the proper conditions with violence. The conditions within the sampling train could easily promote this decomposition - the peroxide would be collected and held on the filter and other surfaces and exposed to the source gas at elevated temperatures during the run. Dienes and other similar unsaturated materials can easily decompose into smaller molecules if the temperature of the train is high enough.

Many compounds including polycyclic aromatic compounds are sensitive to UV light and if exposed, can change chemical composition before analysis. It is essential that all compounds be protected from light during all phases of sampling and analysis.

There are many classes of compounds that can easily polymerize and these polymers could be formed during sampling and/or analysis. Examples of such materials are vinyl chloride, vinylidene chloride, styrene and acrylate esters. If this

polymerization occurred in the sampling system, the material most likely could not be recovered during the cleanup and analysis steps.

The comments and problems outlined briefly here are mentioned to alert those planning to sample organic process streams that it is extremely important to understand the process being sampled and to the necessity of being fully aware of what can happen during a sampling and analysis program. Valid results can be obtained, but not without thought as to what is involved. In general, this manual is directed to those who are experienced in emission sampling. However, included in Appendix I, is a description of some of the considerations required for a successful sampling program and material that has been helpful on past projects.

SECTION II

PRELIMINARY METHODS - LEVEL I

The objective of a Level I sampling effort is to obtain large quantities of sample from a process source in a relatively short period of time with a minimum of manpower. The sample that is obtained can be used to determine the classes or groups of organic compounds that are present and to establish the *in vitro* cytotoxicity and mutagenicity of the stream and stream components. In order to accomplish this objective, methods are defined in this manual for sampling gaseous, liquid and solid phase systems. The methods are intended to apply to many different process feedstock, waste and product streams without major modification. Based on the results of the Level I preliminary survey sampling and analysis program, the requirements for a Level II or Level III program can be defined, and for these studies, the most useful of several optional techniques can be selected.

During the Level I sample acquisition program, process data must be acquired in order to relate the analytical data obtained to the emission rate of the processes. At the minimum, the flow rates and temperatures of each sampled stream must be established. Beyond this, data on the feed rates of raw materials and production rates of the products should be obtained from operation logs and if possible by measurement in order to define emission factors, and to aid in the evaluation of the sampling program with respect to later Level II

and Level III efforts. Regardless of the level of the sampling program, the accuracy and precision of the flow rates and production parameters should be consistent with the accuracy and precision of the sampling technique.

In the following pages of this Section, the sampling methods are defined for Level I surveys of the organic processes in which the sample is contained in a gaseous matrix, an aqueous or non-aqueous liquid matrix, or as a bulk solid. The procedures described are "state-of-the-art" or logical extensions of the "state-of-the-art" and as a result should be highly reliable for meeting the Level I sampling objectives.

2.1 GAS MATRIX SAMPLING

The nature of the organic components in a gas stream depends on the physical properties of both the compounds of interest and the gas stream. The organic components can exist in the solid, liquid, or vapor phase at the condition of the gas stream. As the component is removed from the source, the sampling system temperature and pressure can change the physical state of the component. As a result, one is confronted with the problem of sampling condensed, condensible and vapor forms with the possibility of phase changes occurring throughout the system. Existing sampling techniques provide a means of collecting condensed and condensible species (filter cyclone or impinger collection), but the collection of vapor species presents a particular challenge to the design of efficient sampling systems.

The detection and quantitative measurement of organic components generally requires a concentration step to attain the required analytical detection limits. This is accomplished

with existing systems by sampling for long periods of time and concentrating the condensed or condensible material for this time period on the filters or in the impingers of the sampling system. Some type of concentration step will be required for those materials which exist in the vapor state. This concentration step should collect the material without chemical change and in a form that can be conveniently delivered to the remote analysis location.

The proposed system should collect sufficient material for biological effect studies (a minimum of 50 mg) in a time period of three to five hours with a field team of two to three persons. This requirement eliminates low flow rate sampling systems ($0.02 \text{ m}^3/\text{m}$, 0.75 cfm) and suggests that sampling flow rates of $0.08\text{--}0.14 \text{ m}^3/\text{m}$ ($3\text{--}5 \text{ cfm}$) would be desirable.

In addition to the ability to collect large quantities of material, the Level I sampling system for organic materials should provide the capability of also collecting inorganic materials for a complete evaluation of the source, and provide for size fractionation of particulate matter corresponding to respirable and non-respirable size intervals. These provisions add a great deal of complexity to the sampling system.

Based on this approach, the Level I system ideally should have a sampling flow rate of $0.1\text{--}0.15 \text{ m}^3/\text{m}$ ($3\text{--}5 \text{ cfm}$) provide size fractionation, combine organic and inorganic sampling procedures and yet be of suitable size and weight to be handled easily by several men. A system to accomplish all of these requirements is nearing completion. In order to provide the rationale for such a system, it is necessary to rely on the current state-of-the-art of organic sampling, based primarily on experience with $0.02 \text{ m}^3/\text{m}$ (0.75 cfm) flow rate systems and developments in inorganic sampling with $0.14 \text{ m}^3/\text{m}$ (5 cfm) units.

Under EPA contract 68-02-1393, a technical manual has been prepared for the process measurements of trace inorganic materials.³ The sampling method for Level I described in this referenced manual is based on a high volume stack sampler⁴ and some of the design features of that sampler can be applied to the organic process stream sampler.

In addition, a sampling system has been designed and constructed which has three cyclones in series prior to the filter.⁵ This study provides the necessary background for the proposed size fractionation system for organic sampling.

2.1.1 Proposed Level I Sampling System

In order to provide the entire range of capability desired of a Level I sampling system, it is necessary to combine the triple cyclone approach for size fractionation of particulate, the organic adsorber and the inorganic trace element impinger system. This combined system has not been field tested, but based on laboratory and field pressure drop studies, it is reasonable to assume that such a combined system can be made operational for field use. At present a design and prototype construction study is underway under an EPA contract.⁶

A schematic diagram of the proposed Level I sampling system is shown in Figure 1, and the major component specifications shown in Table 1. The various components and available options that require further description are discussed in the following sections.

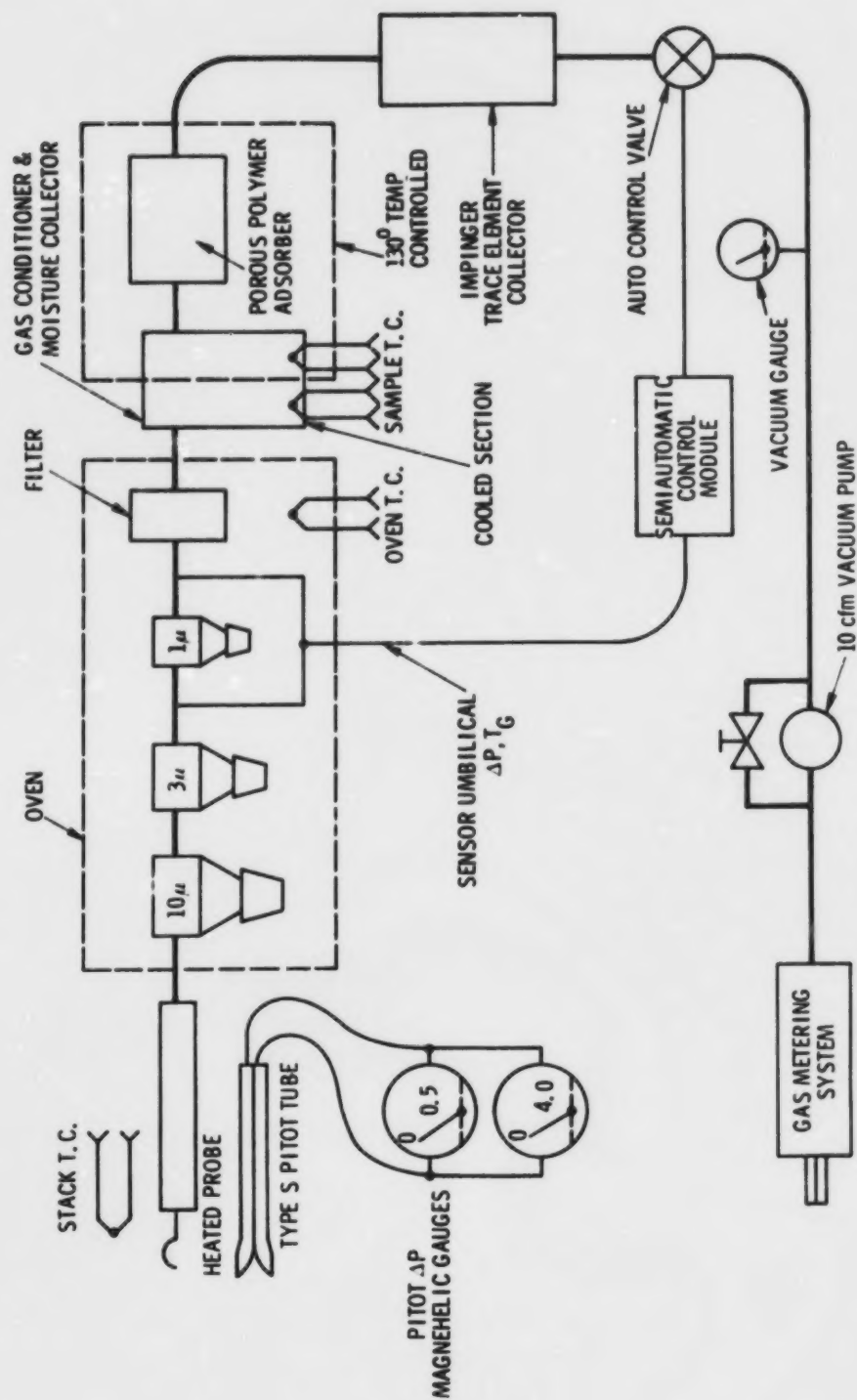


Figure 1. Schematic of Level I Gas Matrix Sampler

Table 1. COMPONENTS OF LEVEL - SAMPLING SYSTEM

Component	Subcomponent	Material of Construction	Specifications
Probe (800°C temp. below 1000°F)	Probe Tips	316 Stainless	Size Range 1/8-3/4" Join to Probe liner - Saegelek Connector
	Probe Liner	316 Stainless	3/4" I.D. Suggested, 1/2" I.D. Optional
	Probe Heater	Resistance Heater	Capability of heating liner to 500°F
	Temperature Monitor	Type K Thermocouple	Compatible to Readout Device or Controller
	Sheath	316 Stainless or Inconel	Sized to contain liner, thermocouple, heater, insulation, and possible stack thermocouple and pitot tube
	Pitot Tube (optional)	316 Stainless	Type S, with coefficient between .80 and .85
Particulate Removal System	Stack Temperature Monitor	Type K Thermocouple	Compatible with Readout Device
	Cyclones - 3	316 Stainless	Aerotherm "stub" cyclones - nominal cut points of 10, 3, and 1 μ m.
	Filter Holder	316 Stainless	To hold 142 μ m. filters, 1/2 or 3/4" Connectors, no teflon coating. Stainless support screen, "O" ring seal if not in contact with gas stream.
	Filter	Quartz (A. D. Little Co.) Type A Fiber Glass (optional) Teflon (optional) As required	Sized to holder, retain particles greater than 0.3 μ m.
	Oven System		Sized to contain cyclones, and filter, capable of 260°C, insulated electrically and thermally.
	Temperature Monitor	Type K Thermocouple or bi-metallic contactor	Compatible to Readout Device, and/or Temp. Controller.
Organic Adsorber	Holder for Adsorber	316 Stainless Steel	Size approximately 90 mm I.D., 20 mm bed depth, Stainless retainer screens, 1/2 or 3/4" inlet and outlet connections
	Adsorber Material	TRUK 7C (Enka V.V., Holland)	40-60 mesh size, preconditioned at 200°C for 24 hours under no flow.
Impingers	Impinger #1	Glass or Lexan	Wet-tip tube of aerotherm design or enlarged impinger of modified Smith Greenberg design - contains 3M H ₂ O, or 4M NH ₄ OH
	Impinger #2 and #3	Glass or Lexan	Modified Smith Greenberg of enlarged design, contains 0.2M H ₂ O, 0.2M HNO ₃ , and 0.02M AgNO ₃ , or 0.2M (NH ₄) ₂ S ₂ O ₈ and 0.02M AgNO ₃
	Impingers #4 and #5	Glass or Lexan	Contains silicon gel if dry test water is used, these impingers connected in parallel.

Table 1 (cont'd). COMPONENTS OF LEVEL I SAMPLING SYSTEM

Component	Subcomponent	Material of Construction	Specifications
Meter Section and Pump	Temperature Display	Optional	Digital Thermometer, thermocouple switch, Readout of Stack, probe, oven, adsorber, exit gas, dry test meter inlet and outlet temperatures.
	Temperature Control	Optional	The probe and oven can be controlled with temperature controller (to 260°C). A number of such units are available.
	Timer		Elapsed time indicator - record to .01 minutes and up to 999 minutes.
	Manometers		Inclined manometers or magnetic gauges for readout of pitot tube SP and orifice meter AH. Read intervals 0.01 inches of water up to 1" water and 0.1 inch above 1 inch of water. Range - 0-6 or 0-10" water, or metric equivalent.
	Dry Test Meter (optional)		Dry Test Meter (Rockwell) of 7 cfm capacity. This unit may be eliminated if calibrated orifice meter and differential pressure readout are employed for total volume determination.
	Orifice	Stainless Steel	Design depends on desired AH reading at various flow rates. Should provide AH of 6-10" of water at 7.5 cfm. Several ranges could be provided for different flow rate ranges as found in Aerotherm unit.
	Pump	Oilless Carbon Van-Type	Capable of 10 cfm at 0" Hg Gast 1022, equivalent - requires 2 1/2 H.P. 1725 RPM motor such as Boerr D272X.
	Vacuum Gauge		0-760 mm of Hg vacuum.
	Valves	Brass, TFE	Shut off valve and control valve. Shut off valve - Whitey B-398 or equivalent. Temperature limitations -20 to 70°C. Control valve - Whitey B-7886 (0.312" orifice) needle valve or equivalent.
	Pitot Lines Sample Lines Power Leads Thermocouple	Polyethylene or Teflon Polyethylene or Teflon 3 wire grounded Type K	Medical cord should be 25-50' lengths with quick connects on lines, grounded plugs and sockets on power lines and Type K thermocouple connectors.

Optional Components - Air Cooled Probes
 - Stainless liners with stainless or inconel jacket
 - Water Cooled Probes
 - Stainless liners with stainless or inconel jacket
 - Cooling Coil
 - Stainless coil and traps to be employed prior to Tenax adsorber.
 - Thermostated Adsorber
 - Tenax adsorber enclosed in water cooled jacket - include ice bath and circulation pump to maintain temperature of adsorber. Suggested temperature 50°C.

2.1.1.1 Probe Tips and Probe Systems

The probe tips and probe for the high volume sampling system are essentially identical to those units used in 0.75 cfm sampling systems. All probe tips should be constructed of 316 stainless steel with round cross sections and knife edges. The probe tip should connect to the probe liner with a Swagelok type connector to provide a leakfree seal. For the most part, the tubing in the sampling system is 1/2" O.D.; therefore, this size is acceptable, however, the use of 3/4" O.D. probe liner and tip connector could be considered to reduced system pressure drop.

The probe liner should be well insulated not only to retain heat from the heating element, but also to provide for safe handling of the probe sheath and eliminate the possibility of electrical shock. The probe liner, heater, probe thermocouple, stack thermocouple, and pitot tube if used, can be enclosed in a single sheath to provide protection for the units and to ease the task of closing the space between the sampling port and the probe.

Ideally, the sampling gas temperature leaving the probe should be a few degrees above stack temperature to prevent condensation of water and condensible organic materials. At the minimum, the temperature should be above the dew point temperature of the gas and, if no water is present, it should be maintained at 50°C (122°F).

For high temperature sources, where glass or quartz are inadequate, stainless steel probe liners must be used. For high temperature sources (above 320°C, or 600°F), air-cooled or water-cooled probes are necessary. As the temperature of various sources reach the 500-600°C range, the thermal

decomposition of organic molecules occurs and much of the emitted organic species may be gaseous and of relatively low molecular weight. Condensation in the probe becomes less of a problem, but collection of gaseous species must be emphasized.

The TRW manual on inorganic sampling suggests that a liner made from a thermally stable polyimide (e.g., Kapton, Trademark of Du Pont Co.) be placed inside the stainless or glass probe liner. This liner is not recommended for the combined organic-inorganic Level I system. If at a later time, it can be shown that the liner is inert in organic sampling, and does not have an effect on the results of biological testing, it may be useful. Stainless steel (316), pyrex or quartz seem the best materials at present for both inorganic and organic sampling and are also suitable for biological testing.

2.1.1.2 Particulate Collection System

This portion of the sampling train consists of the cyclones, filter, and oven components. The original cyclones as discussed in the triple cyclone sampling manual⁵ have been redesigned to fit in an enlarged heated oven. These "stub" cyclones were expected to provide the basic particle size cuts of the original larger units. Based on the data presented in the triple cyclone sampling at ambient temperature (21°C), the D₅₀ values of the cyclones were closer to the desired 10, 3 and 1 µm cut points at 3 scfm than they were at 5 scfm.

The "stub" cyclones were evaluated using 12, 10, 8, 5, 3, 1.75, 0.27 and 0.5 µm mono-dispersed aerosol of ammonium fluorescein.⁷ At 4 acfm, the D₅₀ values for the nominal 10,

3 and 1 μm cyclones were found to be 12 μm , 5 μm and 0.45 μm , respectively. Thus, at the original design flow rate of 5 acfm, the D_{50} values would be approximately 10.5, 4.5 and 0.4 μm . The design of the 3 μm (middle) cyclone, which is typical of all three units, is shown in Figure 2.

At the present time, the experimental "stub" cyclones are constructed of 304 stainless steel, and it is understood that units made from 316 stainless steel will be available within a few months. Blueprints of the cyclone design for those who desire to construct their own will be available from the EPA. Any such units constructed should be made of 316 stainless steel as this material has been evaluated from a toxicological viewpoint whereas the 304 variety has not been studied as yet.

A filter holder for 142 mm diameter filters would be acceptable for the system, however, it might be preferable to eliminate any coatings such as Teflon, applied to provide a non-stick surface for particulate. It is possible that abrasion of this coating surface could occur and thus add to the organic composition of the collected material. The rate of abrasion would depend on the nature of the particulate material.

Quartz filters would be the most desirable, as these materials have the low metals content needed for inorganic analysis. Experimental quartz filter that were at one time available from A. D. Little Co. were excellent, however, commercial quartz filters, in general, have poor mechanical properties. Fiber glass filters may be useful, although it has been found that some commercial lots have varied metals content. This variation is apparently not a problem in the spectrograde fiber glass filters (Gelman Instrument Co.), however, we do

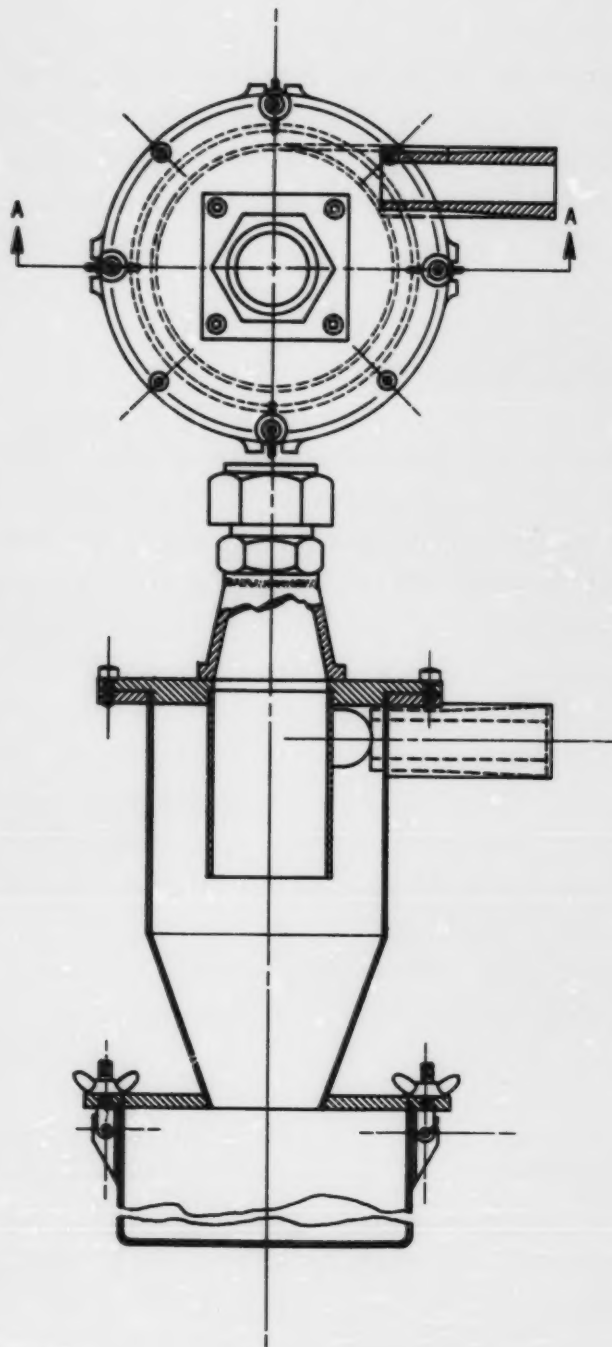


Figure 2. Separator cyclone

not know how this material effects the biological testing results. Teflon filters are also a possibility, but the increased pressure drop experienced with this filter material may create problems with the completely assembled sampling train.

2.1.1.3 Organic Collection System

The main component of the organic collection section of the train is the Tenax GC adsorber. Several options must be considered here, based on the temperature and moisture content of the effluent gases. For relatively low temperature stacks, approximately ambient to 50°C (122°F), it is not necessary to provide a gas cooler, and a very simple adsorber trap can be used. For mid-range temperatures, 50°C (122°F) to about 150°C (300°F), a water-cooled adsorber is suggested. For higher temperatures, a cooling coil-water condenser followed by a thermostated adsorber is required. At this point these temperatures are somewhat arbitrary and may be modified with experience. In each case, it is assumed that probe and oven temperatures are above stack temperature, or at least high enough to prevent condensation in the probes and cyclones or on the filter.

The cooling coil can be a coil of stainless steel (316) with a water collection bottle, arranged so that there is minimal contact between the liquid and the cooled gas. It is suggested that the coil be made of 3/4" I.D. stainless tubing. The water collector should be designed to cause a minimal pressure drop. The Aerotherm gas precooling coil (HVSS-470) is not recommended in the complete sampling system as it has been reported to have a pressure drop of 100 to 152 mm. of mercury.

It would appear that the major contribution to the pressure drop is from the cyclone-type water collector, however, the 1/2" I.D. tubing may also be a factor. By employing 3/4" I.D. tubing and a Tee connection at the lower end connected to a receiver, the pressure drop could be reduced somewhat.

Aerotherm has recently designed a multi-dip tube type of impinger with a water-cooled inner jacket, that may be very useful as a precooler assembly between the heated filter and the organic adsorber. This device will add complexity to the sampling system in that it requires a pump and cooling water reservoir. The multi-dip tube design will aid considerably in the reduction of system pressure drop, but the fact that the device is glass and the sampled gases come in contact with the condensed liquid, may create problems.

The organic adsorber for the system is a scaled up version of the unit used successfully in $0.02 \text{ m}^3/\text{m}$ sampling systems. The adsorber used in lower flow rate systems had a bed depth of 90 mm with a 30 mm I.D., containing about 5 grams of Tenax GC. In order to operate at higher flow rates, the area of the adsorber is increased corresponding to the increase in flow rate. Thus, to operate at $0.1\text{--}0.15 \text{ m}^3/\text{m}$, the I.D. should be about 90 mm, and with the 90 mm bed depth, approximately 40 grams of Tenax GC is required. A prototype of the adsorber constructed of acrylic plastic as shown in Figure 3 has been used to evaluate bed settling and pressure drop effects. For routine use, 316 stainless steel is the material of choice. A proposed design is shown in Figure 4. This unit is suitable for low temperature sources. For mid-temperature operation, a water jacket is required to control the temperature at $50\text{--}60^\circ\text{C}$. A possible design is shown in Figure 5.

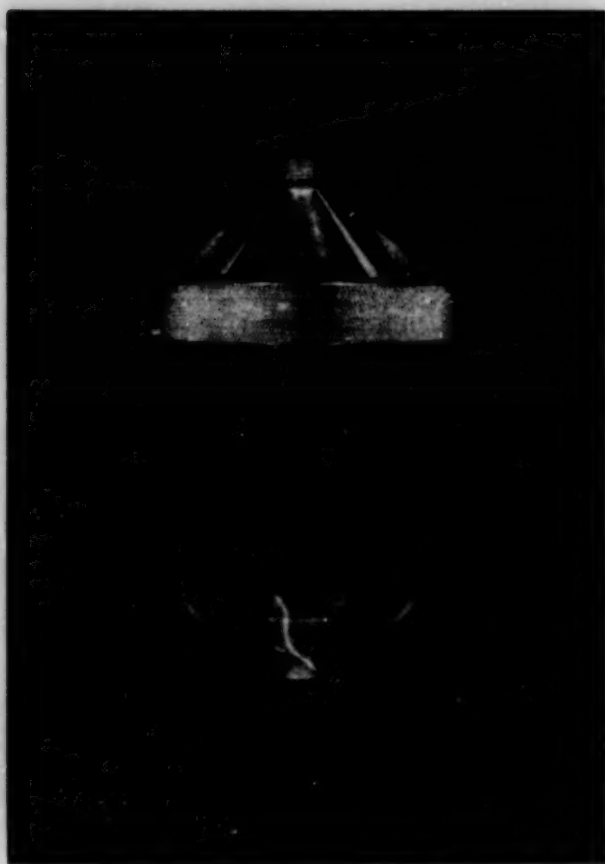


Figure 3. Prototype high volume porous polymer adsorber

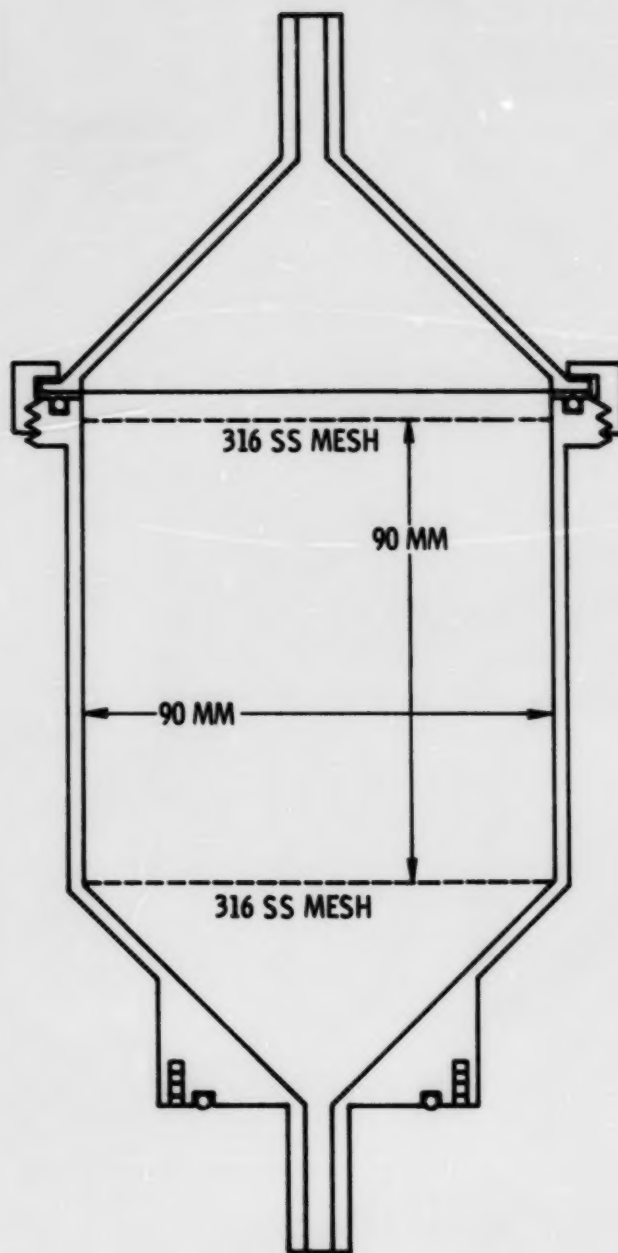


Figure 4. Possible design for production high volume adsorber

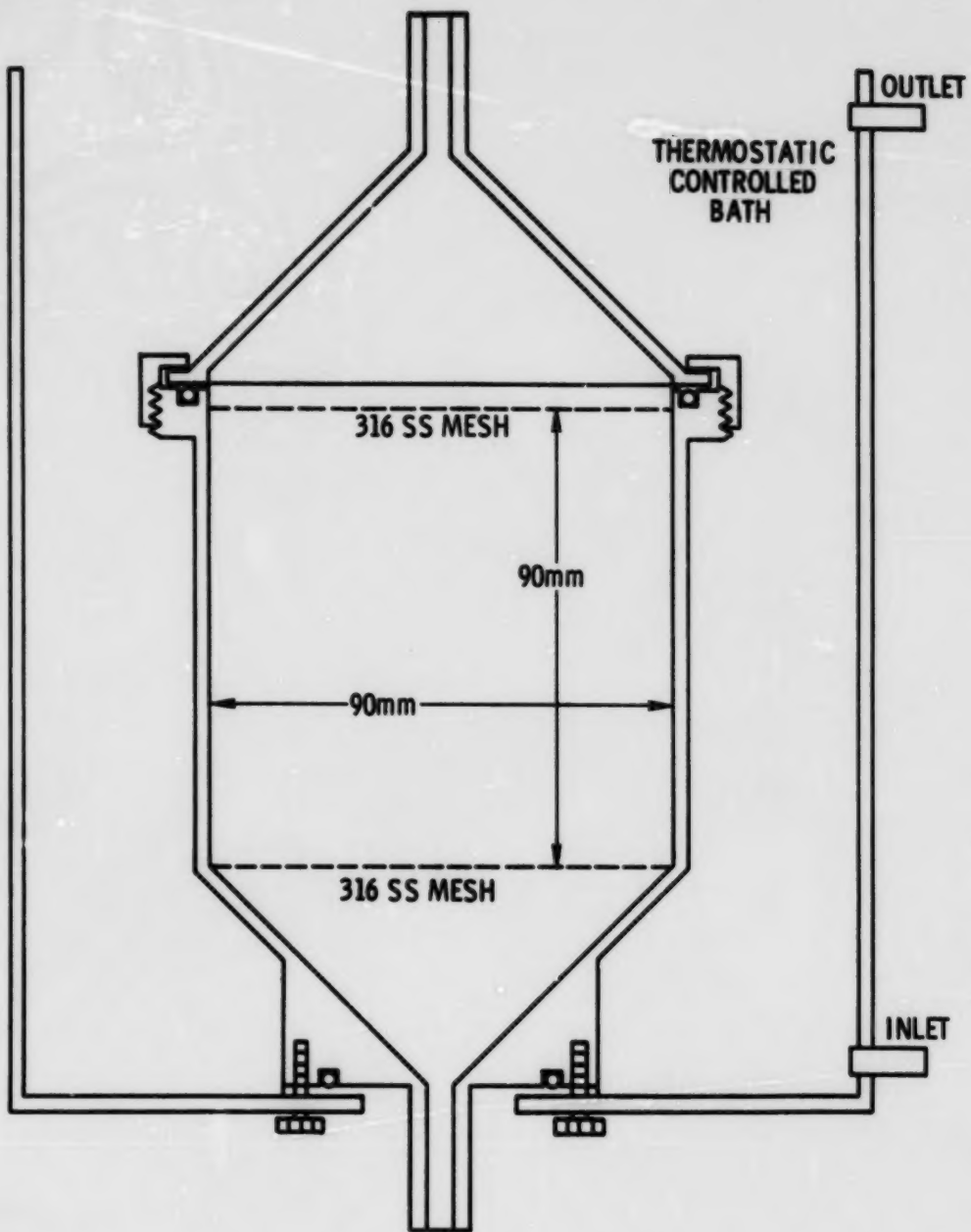


Figure 5. Possible design for thermostated high volume adsorber

The Tenax GC used in the organic adsorber is a material typically used as a gas chromatographic substrate. In the sampling train application, the material is maintained at a fairly low temperature in an effort to enhance the adsorption characteristics of the material. In the chromatographic application, the material is packed into a column. The packed column is operated at higher temperature and with helium flow, the Tenax acts as a selected adsorption-desorption material to separate various organic compounds. This same type of adsorption-desorption phenomenon could occur in the sampling train if the temperature of the Tenax was not maintained at 50-60°C. Further desorption could occur quite readily if the sampling system were operated under high vacuum conditions. The organic absorption characteristics of the Tenax adsorber is, therefore, dependent on maintaining the suggested temperature and system pressures between 0 and 380 mm. of mercury vacuum, and even at this condition some volatile materials will be desorbed from the material. For this reason, it is necessary to employ a supplemental method, which will be discussed in a later section, for the detection of low molecular weight materials.

The current practice on organic sampling is to extract Tenax with pentane in a Soxhlet extractor to remove the organic material. With proper extraction and conditioning the Tenax can be reused. In the combined organic-inorganic sampling system, the porous polymer most likely would trap some of the As, Sb, Se, Cd, Hg, Cl, F, and Pb compounds that would pass through the filter and would be collected in the impingers of an inorganic-only system. This not only means that an additional component must be analyzed, but also that there is a reasonably good chance that the Tenax would be destroyed during the analysis. Even if this were necessary, for a Level I evaluation,

the cost of the Tenax is rather small compared to the cost of sampling and analysis when one considers the information gathered.

2.1.1.4 Impinger System

The impinger section of the sampling train is designed for the collection of inorganic components that can pass through the cyclones, filters and Tenax adsorber. Reference should be made to the inorganic sampling and analysis manual for specific details.³ However, in order to design a Level I system for both organics and inorganics some modification of the system is necessary. As stated in the last section, some inorganic components will most likely be found in the adsorber. Although this will complicate the analysis procedures, it will permit a change in the impinger system to reduce the pressure drop problems.

All impingers used in the system should be of the straight tube design rather than of the Smith-Greenberg type. As a result, the pressure drop in each impinger will be dependent on the liquid level above the inlet tube and will be in the order of inches of water. The nozzle approach of the Smith-Greenberg type impinger is restrictive and adds considerably to the pressure drop.

As will be shown in Section 2.1.1.6, where pressure drop information is discussed, the silica gel impinger, required if a dry test meter is used, adds considerable pressure drop to the system. Two silica gel impingers in parallel can reduce the pressure drop by splitting the flow between the two units. This can be done by providing a Tee in the line ahead of the impingers and then combining the flow after the impingers and before the umbilical cord to the control unit.

2.1.1.5 Umbilical Cord, Control Unit and Pump

The umbilical cord, control unit, and pump from the Aerotherm high volume sampler can be used, or similar units can be constructed. For Level I sampling, a simplified control unit can be built that will provide the minimum requirements. In brief, this can consist of an inclined manometer to monitor the pressure differential across the final cyclone, digital readout thermometer and thermocouple switch, proportional types of probe and oven controllers, and a timer. A dry test meter can be eliminated if a calibrated orifice meter and elapsed time are used to provide volume data. A manometer or magnihelic gauge for pitot tube pressure differential is not required. For the most part, sampling would not be done isokinetically, but rather at a specific rate to maintain the desired flow rate and hence particulate size cut points through the cyclones. If isokinetic sampling were attempted in a system with a wide variation of flow rate profile, the cut points of each cyclone would be varied each time the sampling rate was adjusted. A simplified control unit, therefore, would provide the essentials for Level I sampling at a saving of weight and cost, but it could not be used for compliance or similar testing studies.

2.1.1.6 Pressure Drop Evaluation of Level I Sampling System

During the process of developing the Level I sampling system concept, a major concern was the pressure drop of the various components and complete system. Since the proposed system has not been field tested, there is no assurance that the system will perform as expected. However, Aerotherm has been assembling a sampling train for use on a coal gasification system which included a water-cooled probe, triple cyclones,

filter, and an inorganic-type impinger system. This provided the opportunity to evaluate the pressure drop of this system and, in addition, to add a proposed prototype of the Tenax GC adsorber and measure its contribution to the pressure drop of the system. As a result of this study, it is felt that the system will operate as expected although it could potentially cause some problems in very dirty sampling situations.

The results of the pressure drop studies on both the high volume system and the $0.02 \text{ m}^3/\text{m}$ system are shown in Figure 6. The data plotted in this figure represent the pressure drop in mm of Hg of various components on the complete system against the flow rate in scfm. Curves D and E represent the complete $0.02 \text{ m}^3/\text{m}$ system with and without the adsorber but with Type A filters and charged impingers. With the adsorber in place, flow rates in the $0.008\text{--}0.017 \text{ m}^3/\text{m}$ range are possible, and at these flow rates the initial pressure drops are low enough to permit collection of particulate before exceeding the leak check pressure drop of 15" or 380 mm of Hg vacuum.

Curves A, B and C taken from the data in the TRW report on the Series Cyclone Sampling Train show the pressure drop of this system.⁵ Curve B provides the data on the standard Aerotherm impinger system, charged with liquid as required in the inorganic system. These impingers would create too great of a pressure drop for reasonable operation. Curve C represents data on the cyclone system fabricated by TRW, while Curve A is for the complete TRW-cooler system. Because of the high pressure drop of the impingers, TRW employed the cooler system and substantially reduced the pressure drop across the entire train. Based on these data the system could operate in the 0.04 to $0.14 \text{ m}^3/\text{m}$ (1.5 to 5 cfm) region.

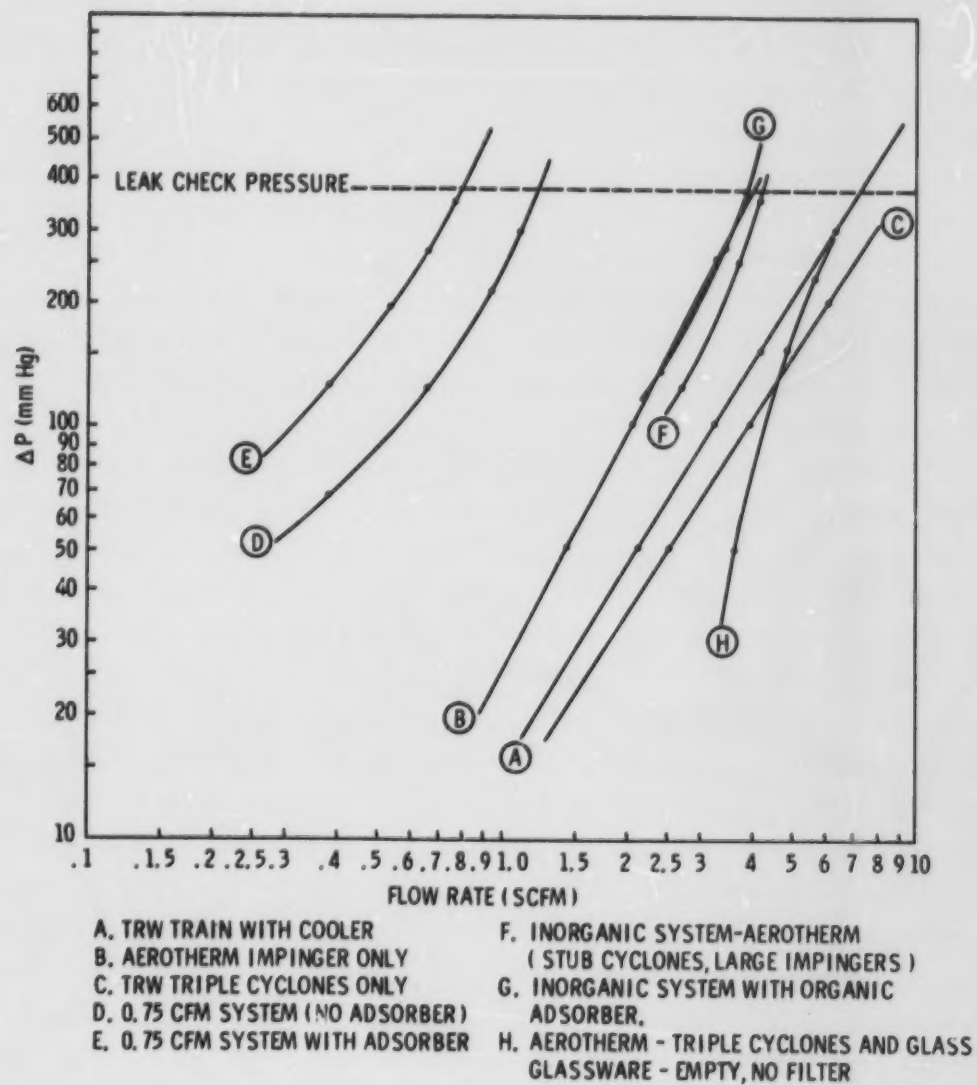


Figure 6. Pressure drop data for various sampling systems

The Aerotherm system designed for the study of particulate emission from the coal gasification facility was employed to determine pressure drop data as a complete system. Various portions of this system were evaluated. The results of several of the measurements are shown in Curves F, G and H. Curve F represents the pressure drop of the complete Aerotherm system, with a 1/2" probe tip, the triple stub Type A fiber glass filter, and the charged enlarged impinger systems. Curve G represents the same system with the prototype Tenax GC adsorber (enlarged unit) in place. These data indicate that a flow rate of 0.085 m³/m (3 cfm) is feasible, but 0.11 m³/m (4 cfm) would exceed the nominal leak check vacuum.

The data show that a major source of pressure drop across the sampling train is the impinger system. A straight tube impinger (modified Smith-Greenberg) containing water can show a pressure drop equivalent to the height of the water above the dip tube and thus would cause a small pressure differential. At a flow rate of 0.034 m³/m (1.2 cfm) the pressure drop would be in the order of 7 mm Hg for a 10 cm water height. The 0.02 m³/m Smith-Greenberg impinger without liquid indicated a 25 mm Hg pressure differential. When filled with liquid the differential was 33 mm Hg. Thus, if at all possible, straight tube impingers are desirable from a pressure viewpoint. Normal impinger operation employs a final silica gel impinger to reduce the moisture content ahead of the dry test meter. If one silica gel impinger is used, this adds 109 mm Hg to the pressure drop. However, by using two silica gel impingers in parallel, this can be reduced to 41 mm Hg.

Thus, for the combined cyclone-organic-inorganic system, it is suggested that all impingers be of the straight-tube design and the silica gel, if used, should be in two parallel impingers. The use of straight-tube impingers will reduce

the collection efficiency for inorganic materials in the impingers, however, it can be assumed that the inclusion of the Tenax GC adsorber in the system should trap these materials with reasonable efficiency, and the impingers would trap the material not collected in the Tenax.

The data indicate that the proposed Level I sampling system could be used successfully in the field to collect both inorganic and organic materials and provide for size fractionation of particulate matter. An $0.085 \text{ m}^3/\text{m}$ (3 cfm) flow rate is quite possible and $0.11 \text{ m}^3/\text{m}$ (4 cfm), feasible. This latter flow rate will provide approximately the desired size fractionation of particulate.

2.1.2 Gas Matrix Sampling - Fugitive Emissions

The material that is blown from bulk storage and conveyors by the wind is of much lower concentration than generally observed in sampling of stationary or confined sources. Ambient air particulate concentrations are sampled by high volume samplers, and this type of device can be used to collect fugitive dust emission for organic analysis.

Another source of organic fugitive emissions is from various plant operations where volatile organic vapors can be released into the air. Sources of these vapors can include transfer operations, leaking valves and fittings, and open areas such as settling ponds. Such materials will not be collected by high volume samplers and are generally present at such low concentrations that sampling is quite difficult.

2.1.2.1 Particulate Emissions

The accepted procedure for either ambient air particulate or fugitive dust sampling is to establish a network of high volume air samplers around the perimeter of the area, which, for fugitive emissions, would be the plant property lines. With the network of samplers, the dust can be collected by one or more of the samplers, regardless of changes in the wind direction and velocity. By relating the wind direction to the sampler location, it can be determined which samplers received emissions from the source and which were receiving "background" dust.

A much simpler system can be used for a Level I sampling program, provided several assumptions are made regarding the meteorological conditions during sampling. In general, if there is no frontal activity in the area of the plant to be sampled, fairly stable weather conditions can be found in the periods from 9-11 am and 1-3 pm. Before 9 am, there is often an inversion; between 11 am and 1 pm, the winds may shift; and between 3 pm and dark, another inversion may take place. For the most part, winds are typically in the 3-15 mph range (90% of the time) which is quite suitable for sampling. Still air (0-3 mph) is typically encountered 5% of the time and is too slow for sampling. Winds higher than 15 mph occur about 10% of the time and also present sampling problems. Winds generally increase during the day and are highest in the afternoon, falling again near dark.

The fugitive emission method for Level I sampling consists of two or three high volume sampling units, one for the background sample and one or two for the collection of the emissions. Sampling should be done only during stable conditions (9-11 am and 1-3 pm). The background sampler is located upwind from

the source and the emission samplers downwind from the source. Sampling duration should be as long as possible and is dependent on the concentration of dust, wind velocity, type of material, etc. If a major wind shift is noted during the interval, the emission sampler should be moved to maintain the downwind location with respect to the source.

A major problem with this procedure is that it is unlikely that sufficient sample will be collected for biological testing, however, the filter can be analyzed chemically and a portion of the material generating the dust source can be collected for both analytical and biological programs.

The type of material collected by this procedure is expected to have a high concentration of inorganic material and a low concentration of organic matter. Volatile organic material will be lost due to the high flow of air across the collected particulate. High molecular weight organic material (such as polycyclic organic materials) would be collected by the filter and the detection of these materials would be an important part of a Level I effort.

A method for measuring the wind velocity and direction will be required for this method. These data, along with the flow rates of the samplers should be recorded routinely during the sampling period. Simple meteorology stations are available from a number of commercial sources or such devices can be constructed that will fit the requirements of the program.

In addition to the ambient air type of fugitive emission discussed above, TRC (The Research Corporation) under EPA Contract 68-02-1815, in their technical manual on fugitive emissions have identified two other types of fugitive sources - those from roof monitors, and those from quasi-stack sources -

which differ mainly in the methods required to obtain samples. Emission from any part of a building, such as windows, doors, open roof sections, vents, fans, etc. into the air is considered in the roof monitor sampling approach. The quasi-stack sampling approach can be employed at any location where a stack-like structure can be built to contain the source.

The roof monitor approach for a Level I study employs high volume particulate sampling systems located within the building adjacent to the openings so as to collect the emission just prior to its entrance into the atmosphere. In addition to the sampler, a flow measurement device (such as a hot wire or rotating vane anemometer) is required at each opening sampled to determine the gas velocity exiting through the opening. The sampler is positioned within the emission "cloud" and the sample collected. The flow device, positioned so it is not influenced by the sampler, and the area of the opening provide a measurement of the emission rate.

The quasi-stack approach is suitable for sources that can be isolated by use of temporary ducting or enclosures. Such sources could include material transfer operations, leaking system components, and open evaporation or fabrication areas. This method generally requires the enclosure, a fan and an exhaust stack or duct. Sampling can be done with any of the typical stack type gas matrix methods and flow measurement devices. For our purpose, the high volume sampling train described earlier should be employed to collect both particulate and gaseous organic materials.

2.1.2.2 Vapor Emissions

The organic vapor emission in the vicinity of a process, even though readily detectable by odor, is generally quite low in

concentration. The ambient air methods for detecting such fugitive emissions are not suitable for a Level I program where both chemical analysis and biological testing is to be done.

The procedures typically employed for ambient air hydrocarbon determination can be used (1) to obtain a total hydrocarbon-less-methane value, and (2) if concentrations are high enough, to provide levels of individual components. These procedures employ a Flame Ionization Detector (FID) chromatograph. This detector combination is very sensitive to hydrocarbons but the materials are destroyed in the flame during analysis and as a result are not retained for other analytical or biological procedures. As this method is more applicable to Level II or III procedures, it will be discussed in more detail later in this manual.

The other possible procedures for organic vapor analysis include the use of charcoal tubes and porous polymer collection. At present, the charcoal tube method is being used extensively for NIOSH sampling programs even though there are some definite problems with the removal of vapors from the charcoal. The NIOSH sampling procedures use a small charcoal tube and a battery powered air pump to draw ambient air through the sample tube. This procedure is generally used for quantitative analysis of specific materials using sensitive instrumental analysis methods. The method is not employed for general identification schemes as required by Level I studies.

For the Level I program, the procedure suggested for ambient vapors is an extension of the Level I stationary source sampling system. In the Level I stationary source system there is a filter and organic vapor adsorber that can be used intact for ambient air samples. By removing the probe and

cyclone assembly (although this could be left intact for size fractionation of air-borne particulate) the sampling train can be operated at $0.11 \text{ m}^3/\text{m}$ near the fugitive emission source to collect the organic vapor materials. This flow rate is an order of magnitude lower than the typical flow rate of high volume ambient air samplers and, therefore, longer sampling periods will be required to provide the required sample. The benefits of this approach are that the sampler is available already for the Level I program and that the methods for handling the sample and completing the analysis are established. Scaling up the organic vapor adsorber to a larger size does not appear practical as long as Tenax or a similar porous polymer is used. This method, at present, is only a concept and has not been tested. There is a reasonable chance that it can provide a sample, at the very minimum for chemical analysis, and hopefully for biological testing as well.

2.2 LIQUID STREAM SAMPLING

The sampling strategies required for the determination of the organic content of liquid streams appear initially to be rather simple, however, there are a number of problems that must be understood if a truly representative sample is to be obtained. As in gas matrix sampling, a sample is extracted from a flowing system, and the determination of an emission rate requires measurement of the mass flow rate of the liquid matrix. In contrast to gas matrix sampling, the liquid may fill only a portion of the duct or pipe. The choice of sampling locations in a liquid sampling situation can be dependent on existing facilities such as manholes or sewer lines, although these locations may not be ideal. Again, in contrast to gas matrix streams, the optimum location for liquid sampling is at a point of turbulent flow. At such locations,

suspended or floating material should be more uniformly mixed and less stratified. Liquid streams at plant locations can consist of either water-based (aqueous) or organic-based (non-aqueous) streams. Nonaqueous systems such as in in-plant ducts and transfer lines are often single phase systems and thus will be the easiest to sample. The organic content of aqueous streams can consist of dissolved, suspended, settled, or floating materials. This type of situation makes the collection of a representative sample a more difficult task.

In this manual, we will restrict our discussion to the sampling of well-defined liquid streams as contained in pipes, ducts or similar systems. No discussion is presented dealing with sampling large bodies of water such as lakes or rivers that would receive outflow from plant sites. This latter type of sampling is much too broad in scope and varied in detail to be covered adequately here.

A Level I program should provide large quantities of material in a relatively short period of time for both chemical and biological testing. The time period must be determined, however, by an analysis of the plant operation and how this affects the acquisition of a representative sample. If the operation is relatively uniform, then a suitable sample can be collected at any time, but if the operation is varied, sampling over a longer period (eg., 24 hours) may be required in order to obtain an "average" sample. Sample preservation is an important consideration. Different materials will require different treatment. This is especially true if both inorganic and organic constituents are to be determined. For Level I, one general preservation procedure is desirable.

The detection and quantitative measurement of organic materials in a water stream can require a field-implemented

preconcentration procedure. This is especially true for aqueous systems where the concentration levels are expected to be low since shipment of large quantities of water is not practical. This type of approach can be employed for dissolved and suspended materials providing that a suitable adsorbing medium and removal solvent is used that does not interfere with the biological and chemical analysis.

Organic matter in aqueous streams can consist of both soluble and insoluble (floating or particulate) compounds. Typically, soluble compounds fall into three categories. The first is materials which are energy sources for microbiota and are considered biodegradable. The second type includes those materials which are toxic to aquatic biota (and humans) and are of major interest in the sampling strategies. The third type are those materials which are neither toxic nor utilized by aquatic biota. The insoluble matter in aqueous streams includes inorganic materials such as process materials, sand, silt or clay, and organic materials such as process material and living or previously living matter. Such materials are in the form of a suspension in turbulent flowing streams, but tend to settle in slow moving streams or pools, and the resulting two-phase system complicates the sampling program.

As part of the Level I sampling scheme, it must be assumed that little information is available on the concentration levels of the organics materials and a strategy is used which will provide suitable samples over a wide concentration range. In addition, the potentially low concentration of organic material in aqueous streams requires that extreme care be exercised to prevent contamination from any source.

The sample size requirement for typical wastewater analysis indicates that volumes up to 1 liter usually are sufficient

for anion and cation analysis, physical tests, and dissolved gases. However, the determination of oily material can require volumes up to 5 liters just to obtain a weighable quantity of extracted material. This quantity could be sufficient for chemical analysis but not for additional biological testing.

2.2.1 Level I Sampling Schemes

At the present time, the procedures that have been published in the Federal Register are concerned with the analytical methods to be employed in water sampling programs. Such procedures are given in the October 16, 1973 Federal Register.⁸ Sampling methods are outlined in various ASTM procedures including D510-68 "Standard Methods of Sampling Industrial Water," D1192-70 "Equipment for Sampling Water and Steam," D860-J4 (1972) "Sampling Water From Boilers" and D1496-67 (1972) "Sampling Homogeneous Industrial Waste Water." Several other sources of sampling methods include "Standard Methods for the Examination of Water and Wastewater"⁹ and the EPA publication "Handbook for Monitoring Industrial Wastewater".¹⁰ A review article by Rabosky and Koraido that covers both sampling and flow measurement can be found in Chemical Engineering.¹¹ All of the above references and most of the information that is readily available from other sources are concerned mainly with aqueous streams.

The wide variation in organic component concentrations in liquid streams suggests that two methods are required for a Level I Sampling Program. The grab sampling approach will be appropriate for process streams and effluent streams where the concentration of the organic material is known or, based on the presurvey, expected to be high. It is difficult to

define exactly what is meant by a high concentration, however, as a general rule, if the components present can be easily detected by the analytical procedures in 1-5 liters of liquid, then this procedure should be used. However, if the concentration is expected to be low and trace organic compounds are of interest, then a concentration procedure is required. Grab sampling does require the transportation of large quantities of liquid, maintained at a low temperature (for preservation of the sample), and this presents some logistics problems. As the concentration levels are unknown at the beginning of Level I program, it would be logical to collect both grab and field-concentrated samples.

2.2.1.1 Grab Sampling Techniques

For a Level I study, a grab-type liquid sample rather than a composite sample should be suitable. It must be understood that a grab sample can only represent the conditions present when the sample was taken, but if the process is relatively constant, or if a time is chosen that would indicate possible worse case conditions, the sample would be acceptable. For a Level I grab sample, mechanical collection would be an unnecessary complication, and therefore, manual collection of the grab sample will suffice.

The following list provides some of the more important criteria for collection of grab samples from aqueous streams:

- (1) Sample containers should be of Teflon with Teflon-lined screw caps. Alternatively, if Teflon is too expensive, glass bottles (wide-mouth) may be used. Polyethylene or polypropylene bottles should not be used for

organic sampling due to possible contamination. One- to two-liter bottles are convenient.

- (2) All glass bottles and caps should be cleaned with chromic acid cleaning solution, concentrated HCl, tap water, and 3 rinses of distilled water. Caps and Teflon bottles should be cleaned with detergent instead of the cleaning solution, followed by tap water and distilled water.
- (3) A site for sampling should be located where turbulent flow exists so that solid matter is well suspended in the medium.
- (4) While one- or two-liter bottles are indicated for handling convenience, it is suggested that at least 2 liters and preferably 5 liters be collected.
- (5) Immediately after sampling, bottles should be cooled to about 4°C, placed in the dark and shipped to maintain this condition. Analysis should be done as soon as possible, and the time between sampling and analysis noted.

The mechanics of the grab sample collection will vary with the physical layout of the site. If the liquid stream is readily accessible, the sample bottles could be filled with the liquid directly. This type of approach could also be used for nonaqueous sampling of process streams by employing sampling taps if such taps are available for plant quality control analysis. In this case, it must be determined if the temperature and other conditions of the stream are compatible with the sampling vessel.

If the physical layout of the site is such that direct sampling is not feasible, then other methods of withdrawing the sample will be required. One such device is a long-handled stainless steel dipper that can be lowered into the stream to extract the sample. Another device is the Sirco Uniscoop Liquid Sampler which is similar to the dipper but has a manually operated ball valve which can be opened to admit a sample after the device is in the liquid stream. Other possible schemes would require a hand- or motor-operated pump to withdraw a sample. The choice of hand operation or one of the various motor-driven units would depend on the distance from the operator to the stream and hence the hydrostatic head of liquid required to reach the sample container. While a number of automatic samplers are available, the use of such devices generally would be more appropriate in Level II or III sampling programs.

2.2.1.2 Field Concentrated Sample Collection

Based on the current state of the sampling art, the Carbon Adsorption Method (CAM) provides a procedure that can be used for the identification of classes of organic compounds present in an aqueous stream. Although this method has been employed for a number of years, there are a number of problems that must be considered.

Two carbon adsorption methods have been employed depending on the nature of the stream to be sampled. The high flow method, used for clean drinking water systems, collects the organic components in 19,000 liters of water at a flow rate of 1 l/m over a 14-day period. This method is not suitable for streams with a high suspended solids content. The low flow CAM employs a flow rate of 120 ml/min for typically a one-week

sampling period to collect organic components from a total of 1200 liters of water. Because of the high flow rate, the collection efficiency of the high flow system is not as good as in the low flow system. Both methods suffer from the lack of complete recovery of the organic components by solvent extraction of the carbon.

The carbon from the CAM procedures are extracted with chloroform and the carbon chloroform extract (CCE) is evaporated and weighed to determine the total organic contamination in the water. In the Dec. 24, 1975 Federal Register¹², some of the problems of the CCE as an indicator of the health effect of organic chemicals are discussed. First, the CCE accounts for only a fraction of the organic components. Second, there is a serious question as to the reliability of the method in identifying toxic materials. Third, there are no data available for establishing a specific level for the CCE on a rational basis. Finally, chloroform is suspected of possessing carcinogenic properties.

The CAM sample can also be subjected to an ethanol extraction procedure. This is termed the carbon alcohol extract (CAE). It would be expected that additional compounds that have little or no chloroform solubility could be removed from the carbon with this solvent. Typically, both extracts are reduced to dryness and the weights used to obtain the organic content. As a possible variation, both the CAE and CCE could be employed for chemical analysis without complete solvent evaporation to provide some information on the nature of compounds present in the water.

The many problems associated with carbon adsorption and subsequent incomplete removal of the adsorbed species has prompted investigation into other substrates. Polyurethane foam¹³,

XAD-2 resin¹⁴, and porous polymers¹⁵ have been tried on a limited basis. For the most part, the applications of these materials have been restricted to concentration steps of existing water samples prior to analysis and not to field use as a sampling substitute for the CAM technique.

The application of porous polymer materials for the collection of organic species of air samples has developed to the point where it is used routinely and good separation techniques for removing the materials from the polymer are available. The technique of employing porous polymer to remove organic materials from water samples in the laboratory prior to analysis appears to be very successful. A very desirable Level I technique, therefore, would be to develop an on-site sampling device that employs this approach. At present, this is beyond the state-of-the-art, however, it is conceivable that the porous polymer could be used in place of the carbon in a modified CAM sampling system. The basic system would consist of a probe to reach into the liquid stream, a porous polymer filled adsorber and a pumping system. There are a number of unanswered questions and additional research is required to determine: (1) the diameter and length of the adsorber, (2) the flow rate for efficient collection, (3) length of time required to collect sufficient sample without breakthrough of the compounds of interest, (4) the pumping requirements of the system, and (5) the collection efficiency of the porous polymer for the organic compounds of interest in a water matrix. The existing evidence clearly indicates that the method has a great deal of promise, but at the present time the uncertainties tend to preclude the recommendation of this technique as the prescribed Level I approach. As a result, it is suggested that the established CAM technique, with its inherent problems, be employed, but that the

feasibility of the porous polymer method should be investigated and hopefully, in time, it could replace the older procedure.

By employing the CCE from a CAM sample as a measure of the approximate organic content, it is possible to calculate the time requirement for sampling. Typically, clean ground waters have CCE values of about 25-50 $\mu\text{g/liter}$, and drinking water with a CCE value above 200 $\mu\text{g/liter}$ has objectional odor and taste.¹⁶ For nonpolluted water, the CAE value may be less than 100 $\mu\text{g/liter}$, and in polluted water the value could be 200-300 $\mu\text{g/liter}$. For fresh industrial pollution, the CCE typically exceeds the CAE, however, for other types of water, the CAE may be several times higher than the CCE. If we assume that the CCE for a typical plant effluent ranges from 100 μg to 1000 $\mu\text{g/liter}$, at the typical flow rates of 0.25 gal/min (≈ 1.0 liter/minute) approximately 0.7 to 7 days would be required to adsorb 1.0 gram of chloroform-extractable material. Further, if it is assumed that the CAE value is the same as the CCE value, 0.35 to 3.5 days would be required to obtain 1.0 gram of total extractable organics. This would indicate that a high flow technique would definitely be required for Level I sampling.

The suggested approach for the field concentration sample collection would, therefore, be to employ the high flow procedure, using flow rates of 1 liter/min and sampling for periods of four to twenty-four hours. As this period is shorter than the typical 14 days and less than 19,000 l. are sampled, there is less likelihood that clogging of the filter with suspended material will occur during this shorter time period. The procedure will depend, however, on much more complete removal of the adsorbed organic species from the charcoal in the analytical phase of Level I sampling.

Details of the method can be found in the "Standard Methods for Water and Waste Water"⁹ under Procedure 139, "Organic Contaminants". A review of the technique and some of the modifications that have been attempted can be found in Chapter 11 of the "Water and Water Pollution Handbook".¹⁶ In brief, the carbon adsorber is a 3" I.D. pyrex tube 18 inches long with end caps to fit 3/4" stainless steel pipe. The end caps are also provided with 40 mesh stainless steel screen to contain the carbon adsorber. Two mesh sizes of carbon, 4 x 10 mesh and 30 mesh, are required for the adsorber. The 4 x 10 mesh is added to the tube to a depth of 4.5 inches and 30 mesh to a depth of 9 inches. The remainder of the tube is filled with 4 x 10 mesh. The carbon adsorber is compacted by gentle tapping. All pipe joints in the connections to the source should be made with stainless steel pipe (rather than the galvanized pipe specified in the methods) and Teflon-type tape, avoiding other types of pipe joint compound. To collect the sample, the water flow is started, slowly at first, then up to the 1 liter/min flow rate after several minutes. This flow rate is then continued for the specified time intervals. It would not be essential to monitor the total volume for a Level I screening study, but if possible a meter would be useful in determining the concentration of organic materials. After the specified time interval, the carbon adsorbing unit should be sealed with stainless end caps and the unit held at about 4°C for shipment to the laboratory. From this point on, the procedure for analysis would be similar to the extraction procedures employed for the porous polymer from air sampling, presented in the Analytical Methods manual prepared by Battelle Laboratories¹⁷ rather than by the procedures for the CCE and CAE in "Standard Methods"⁹.

The carbon adsorber and other sampling components can be easily constructed, however, they are also available from commercial sources such as General Metal Works, Cleves, Ohio.

The affinity of carbon for organic materials requires that a great deal of care be exercised in the use of the CAM technique to prevent contamination of the samples. The carbon must be of high purity and must not be exposed to any organic vapor during manufacture, shipping, or laboratory handling. Ideally, the laboratory where the adsorbers are handled should have ventilating systems that are isolated from any organic sources and all other laboratories. It is essential that carbon blank samples be carried through any operations and analysis in an identical fashion as the samples.

2.2.2 Level I Liquid Flow Measurements

Accurate measurements of the flow rate of streams in pipes and ducts are rather complicated and generally not required for a Level I study. As quantitative data are limited in a Level I study, only approximate emission rates would be possible even if reliable flow data were obtained. It is suggested, therefore, that an approximate flow be determined if this can be done in a simple manner.

Since the requirement for the examination of waste streams by the plant personnel for internal or state agency use is becoming more common, it is likely that flow measurement devices will be found at many plant sites. Whenever possible, existing facilities should be used.

In the event that flow measurements must be made on a Level I study, methods should be chosen that are low in cost and that will not require the installation of complex hardware.

Simple procedures that can be employed include: (1) reading of inlet water flow meters, if such a meter is directly related to the effluent stream of interest, (2) capacity of pumps in the system, (3) a bucket and stopwatch, to time the interval required to fill a bucket of known capacity. (4) the use of floating objects or dyes, by timing the interval required for the object or dye to travel the known distance from one point to another. The accuracy of these methods varies from fair to good and no one procedure is appropriate to all systems. Other procedures that are described later under the Level II and III approaches can also be employed.

2.3 SOLID SAMPLING STRATEGIES

Defining a Level I sampling scheme for solid materials is not a simple task. The sampling of bulk materials is concerned with (1) the raw materials and fuels that are used in the process, (2) the materials that are transferred or produced in the process, and (3) material that may be collected as solids in control devices such as baghouses, electrostatic precipitators and cyclones. Each of these situations presents a different problem in the acquisition of a representative sample.

Raw materials and product solids can be found in large piles, as in open storage, or contained in hoppers, silos, or rail and highway vehicles, or in flowing streams including pneumatic transfer lines, process conveyor systems and bucket type elevators. The choice of the sampling approach is dependent on many factors such as accessibility, the physical layout of the system, the physical properties of the stream and the degree of accuracy and precision required in the sampling, flow estimation, and subsequent analysis. Fortunately

for the purposes of Level I programs, many facilities maintain some type of quality control program on both raw materials and products and thus suitable Level I sampling sites may be available.

In general, the collection of material from control devices is often ignored, unless a material balance type of program is being conducted, or the material represents a useful product. Most often the material is simply removed and disposed of, either to another plant or as waste. As a result, the material in a baghouse or ESP or from a cyclone may not be accessible. Special arrangements with plant personnel must be made to obtain such samples.

The basic procedures for sampling solid materials can be obtained from various ASTM procedures. These techniques are usually specific for certain types of non-organic materials, however, the procedures can be applied to almost any type of bulk or solid sampling situation. "Standard Method of Sampling Coke for Analysis" ASTM D346-35,¹⁸ while designed for gross samples, provides the techniques for the alternate shovel and coning and quartering methods and defines the location of sampling points from the exposed surface of transportation vehicles.

ASTM D1799-65 "Sampling Packaged Shipments of Carbon Black,"¹⁹ provides a procedure for sampling bagged or cartoned materials. Method C183-71 "Sampling Hydraulic Cement,"²⁰ provides a method for obtaining samples from bulk storage at a point of discharge and also provides the design of a slotted tube sampler for hopper sampling. A similar slotted tube sampler is described in D2617-72 "Sampling Particulate Ion-Exchange Materials".²¹ Several mechanical sample dividers and riffles

which can be used to collect or reduce the size of a sample are shown in D2013-72 "Preparing Coal Samples for Analysis".²²

Three other ASTM reports of interest in sampling are E105-58 "Probability Sampling of Materials"²³, E141-69 "Acceptance of Evidence Based on the Results of Probability Sampling"²⁴, and E122-72 "Choice of Sample Size to Estimate the Average Quality of a Lot or Process"²⁵.

The methods required for sampling of solid organic materials can be, for the most part, adaptations of these procedures. The equipment and methods, however, must be tailored to the vessel or site to be sampled as well as the material.

The problems associated with this type of sampling is more dependent on the physical nature of the material rather than the chemical composition. Materials in powder forms exhibit many unique properties. If such powder is compacted by vibration and pressure, it can exhibit some of the characteristics of a solid body. If the powder contains well-rounded particles that are graded in size, it can flow like a liquid. If the powder is very fine, it can aerosolize to form a gas-like system. Solid material in a moving system tends to segregate by particle size. Thus the job of obtaining a representative sample is complicated. Segregation will occur whenever one part of the powder moves relative to other parts. The large particles generally will be found throughout the samples, but the finely divided material will tend to be collected at the bottom of the conveyor belt or other moving stream. In any sampling situation where the material is moved, the sample must include the full cross-section of the material in order to obtain both coarse and fine material.

When solid material is poured into a heap, the larger particles tend to be found at the rim of the heap. The center of the heap may be completely devoid of large particles. This effect can also occur in a hopper or bin. When the bin is opened, the initial flow may consist of only fine material. In practice, this effect is minimized by employing steeply angled hopper designs.

Another effect that can be observed with powdered materials is termed "bridging", and this effect is readily noted in vertical pipes. The particles can "bridge" across an opening that may be as large as ten times the particle diameter. When this occurs, flow will cease. This effect is well-known in plant design engineering. However, it is an effect that also can occur during sampling if the sampling equipment is designed with openings that are too small.

Another interesting property of a powder is that the flow rate of a powder through an orifice is independent of the head of solid above the orifice. This is in contrast to liquids where the flow rate is directly dependent on the hydrostatic head.

Fugitive emissions can be encountered when solid materials are stored in the open or during transfer of solid materials from one vessel to another in such a manner that air currents blow across the material. This situation has been discussed under the gas matrix sampling strategies.

The concentration of the organic components in a solid sample can vary from trace concentrations to 100%. As a result, the sampling procedures must include a consideration of the concentration levels expected, the sensitivity of the analytical procedures, and mass requirements for biological testing

programs. This complicates the specification of a sampling method, and some judgment will be required on the part of the team members to collect sufficient sample for all required procedures.

The wide variation in possible sources to be sampled requires that a description of many possible methods be considered and that the choice of which method is to be used depends on the situation. In the Level I approach, these samples are mainly of the "grab" type. As a result, the restrictions inherent to this type of sampling must be considered.

2.3.1 Level I Sampling of Bulk Material

For this type of situation, equal portions of material at random locations should be removed from the pile. These portions can then be composited to obtain a single sample. If at all possible, each portion should represent the full depth of the material so that the effect of powder segregation can be eliminated. Suitable sampling devices include a pipe borer, slotted tube (thief), or auger, the choice depending on the physical condition (such as moisture content, particle size, degree of agglomeration, and hardness) of the material. If the resulting composited sample is larger than necessary, the sample for analysis can be reduced in quantity by the alternate shovel, and coning and quartering methods.¹⁸ The sample should be packaged in clean glass or polypropylene bottles for shipment. For this type of sample, plastic bottles should be satisfactory unless there is some reason to believe that the material can be contaminated by plasticizer or other components present in the plastic.

The slotted tube type sampler can also be used to obtain samples from packaged materials. In this case the sampler should be inserted diagonally through the bag of material. A similar approach is suitable for sampling from bulk shipments contained in cars and trucks. The usual approach is to take three samples from well-distributed points in the bulk of material. Devices for sampling packaged materials and from bulk shipment vehicles are given in the ASTM procedure for "Sampling Hydraulic Cement".²⁰

2.3.2 Level I Sampling of Moving Solid Materials

The sampling procedure specified for a moving solid stream is dependent on the nature of the design of the transport system. The simplest system is an open conveyor belt where material such as coal, aggregate, or simpler material is transported from a pile to another vessel. A critical point to remember is that segregation is going to occur, therefore, a sample must include a complete cut from the surface of the solid through to the conveyor belt. The initial approach is to employ the "stop belt" procedure, which involves stopping the conveyor and removing a sample of the full cross-section of the solid. This method is practical only if it will not disrupt the production schedule of the plant. The important criteria for this sample are: (1) the full cross-section cut with parallel sides is removed from the stream, and (2) the distance between the parallel faces should not be less than three times the diameter of the largest piece of material.

If the "stop belt" procedure cannot be used, it is not recommended that a grab sample be removed from a moving belt. Not only would this method yield an unrepresentative sample due

to the segregation effect, but also this method is an unsafe procedure, and safety must be a prime consideration around moving machinery.

The best procedure for removing a sample from a moving belt is moving a cutter device entirely across the stream at a uniform speed. The speed of this cutter should be designed to minimize disturbance of the material and thus reduce the amount of segregation. The major problem with this approach is that it requires a cutter device that is designed for the specific velocity of the stream of interest, and the cutter is often built into the system to be sampled. Thus, this degree of complexity is not usually appropriate for a Level I study. If such a device is available for quality control purposes, it should be used. The criteria for this device are given in ASTM D2234-72 "Collection of a Gross Sample of Coal".²⁶

The collection of a sample from the discharge point of a bin or hopper can be accomplished for a Level I program if access is available. The procedure involves moving a pan across the discharge so as to accept the entire cross-section of the material, without overflowing the container. It is desirable to collect three random samples from each hopper, avoiding the initial discharge. Less segregation will be apparent in nearly full bins. At times this procedure will require the construction of the sampling system and in this case is not appropriate for a Level I program.

There are also a number of reciprocating cutters, rotating cutters, and riffle type devices that are employed for sampling. These devices must be installed in the system and thus are not appropriate for Level I sampling programs. If they are available, however, they should be used.

2.3.3 Material Collected by Control Devices

For certain types of environmental and process studies, the material collected by the baghouse, ESP units, or cyclones are of significance in order to completely characterize a process. The material deposited in the baghouse or ESP can be sampled by grab techniques during a shutdown. It is suggested that material be collected from a number of areas in order to obtain an "average" sample. Cyclone devices provide two sources of solid material, both of which are entrained in a moving air stream. The fine material emitted from the outlet can be sampled by typical gas matrix sampling methods, while the heavier material from the bottom of the unit is more typically sampled by moving stream solid samples or gas matrix procedures, depending on the air/solid ratio.

SECTION III

LEVEL II AND LEVEL III SAMPLING STRATEGIES

At the completion of the Level I sampling and analysis program, it is expected that basic information on the physical composition of the process stream will have been obtained, the classes of chemical compounds present will have been identified, and the material collected will have been evaluated to determine its cytotoxicity and mutogenicity properties. At this point, an evaluation of the data would indicate if sufficient data to assess the source is available. Based on this evaluation, a decision can be made to terminate the study of this source or to continue to the more complex Level II or Level III programs.

This chapter discusses methods that can be employed if Level II or Level III studies are indicated. To review, a Level II program is an extensive qualitative, semiquantitative approach to identify specific substances that exist in streams having a significant environmental impact. At the conclusion of Level II, the physical, chemical and biological characteristics of the stream should be well understood under "normal" operating conditions. Level III is a quantitative study of the effect of process variables on the emission rates of specific substances that have been identified as appropriate indicators of the environmental impact of the process streams. The indicators to be chosen are identified in a Level II study. As a result, a Level II evaluation must be done before

a Level III study or, if potential indicators can be identified before sampling. Level II and Level III sampling programs can be done concurrently.

In the previous chapter of this manual, Level I sampling methods were specified for each of the various sampling situations. It is expected that these methods will be used without major deviations in an effort to standardize the procedures over a wide variety of source types. In the Level II and Level III approach, more flexibility is required in the methods; the methods should be specific for the material to be analyzed and for the site to be sampled. As a result, there is considerably more judgment required in the selection of sampling methods. Therefore, a number of potential procedures are presented in this manual that have been or may be used. The choice of methods will depend on the objectives of the sampling program, the nature of the chemical compounds, the physical layout of the sampling site, and the accuracy and precision desired in the data.

In the Level III program, detailed information on the process and process variables must be obtained during the sampling effort. This requires complete cooperation between the plant personnel and the sampling teams, and in addition, the ability of the sampling group not only to sample the emissions but also to measure the process conditions as they vary during the program.

3.1 GAS MATRIX SAMPLING STRATEGIES

Organic air emissions occur in the condensed, readily condensable, and vapor forms. Of these, only the vapor form presents a serious challenge to the design of efficient sampling and

concentration approaches. In general, the condensed organic species can be removed by filtration of an integrated sample over a period of time sufficient to satisfy the detection limit of the analytical procedure. Similarly, readily condensed species can be sampled employing trapping procedures at ice or dry-ice temperatures with care taken to avoid loss of material by microfog (submicron aerosol) formation. Trace organic vapor species generally require a concentration step to attain the required detection limits. The most frequently employed concentration techniques are solvent scrubbing, condensation (cryogenic trapping), adsorption on activated carbon, chromatographic equilibration, chemical reactions, and chromatographic column trapping.

3.1.1 Stationary Source Methods

By far the simplest technique to obtain organic emission samples is grab sampling or some similar approach in which the sample is collected slowly over a time period. The sample is drawn from the source with a glass sampling bulb or into an inert bag (such as Tedlar or Teflon) as shown in Figure 7 and the entire contents are analyzed for organic materials. Typically, a particulate filter is used prior to the sample vessel; this will also remove condensed species. As the vapor at duct temperature is usually cooled in the collection device, material will condense on the walls of the container and thus may not be removable for the analytical device. The quantity of collected material is small and not sufficient for determination of low levels of materials or for biological testing. Reactions can occur within the sample and the results of the analysis may indicate materials that were not in the gas stream. Leakage is a major problem with these devices. This approach might find utilization as a secondary collection

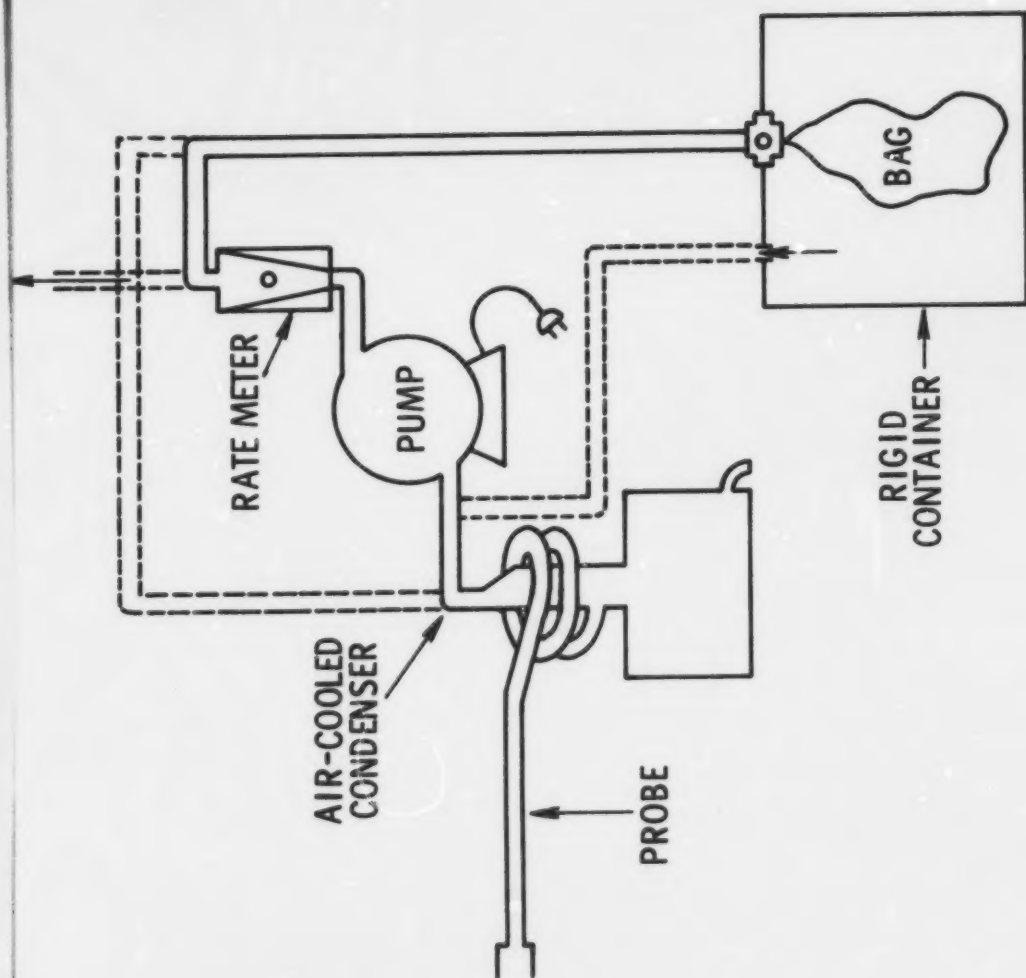


Figure 7. Integrated gas sampling train,
 (Solid lines showing normal arrangement,
 Dotted Lines - alternate arrangement,
 evacuating chamber around bag.)

procedure for low molecular weight gases that could easily pass through other collection devices, but generally the procedure is not recommended.

One other application for this type of sampling is in the use of an on-site chromatograph with a flame ionization detector. Suitable units are commercially available that are truly "stack portable" and thus provide for the analysis of methane and total hydrocarbon measurements on-site or with the proper columns and detectors for specific classes of volatile compounds.

Such on-site chromatographs can provide semiquantitative analysis of specific compounds provided that calibration data are obtained using the proper columns and detectors. Compound identification is accomplished by the use of retention times. This technique, while not providing absolute identification, is usually reliable. Examples of compound classes that can be sampled and analyzed by this technique along with the detector and typical column are given in Table 2.

Table 2. DETECTOR-COLUMN OPTIONS FOR THE GLC SEPARATION OF VARIOUS CLASSES OF ORGANIC MATERIALS²⁷

Class	Detector	Column
Aliphatic Hydrocarbons	Flame Ionization	Chromosorb 102
Sulfur containing	Flame Photometric	15% UCON-50 on Chromosorb T
Alcohols	Flame Ionization	5% Carbonwax on Chromosorb WHP
Acetates	Flame Ionization	5% Carbonwax on Chromosorb WHP
Chlorinated Compounds	Flame Ionization	10% DC200 on Chromosorb WHP
CO, CO ₂ , N ₂ , CH ₄	Thermal Conductivity	Molecular Sieve

This list is not all-inclusive; many other useful columns and detector combinations can be found in the literature.

3.1.1.1 Solvent Scrubbing

Solvent scrubbing for organics is achieved using an impinger train containing a solvent system or combination of solvents which will trap the desired emissions. The train is often held at ice temperature to enhance collection efficiency and minimize loss of the desired components. Depending on the concentration of the emission, the flow rate and the sampling time, the solvent must be reduced in volume to concentrate the pollutants before analysis. Evaporation of the solvent runs the risk of significant losses in the more volatile components of interest.

This type of approach was employed in the earliest studies for organic materials. Typical particulate systems were employed to collect the inorganic particulate and condensed organic materials on the filters. Those materials that were in the vapor phase at the filter temperature passed on through the filter. Those organic materials that could condense at the impinger temperature were collected in the impingers of the train. The actual gas temperature would depend on cooling efficiency within the impingers and could be as high as 21°C (70°F) and still meet the method criteria. Materials that condense in the 21-100°C (70-212°F) temperature range may be collected, but low boiling point materials and those with high vapor pressures would most certainly be lost. The procedures require that the impingers be filled with water. The organic materials will be found in the water, the acetone rinsings of the impingers and later during laboratory work in the water or chloroform-ether extract of the water phase.

Results with this procedure were very disappointing. Often a major portion of the collected material was found to be silicone grease used to vacuum seal the impinger glass-to-glass joints.

Another approach was to employ different collection media in the impingers, such as toluene, xylene, methylene chloride, etc. Silicone grease could be eliminated in favor of water seals, Teflon seals, Spectrovac grease, or ground ball joint seals. The approach may be quite useful for specific organic materials if the collection efficiency of the impinger solution is known for the compounds of interest. It may be the best approach for some materials, such as aldehydes, which present difficulty in the more generalized sampling schemes. The sampling train for aldehydes shown in Figure 8 is typical of impinger collection systems.

3.1.1.2 Condensation Techniques

Use of condensation techniques is one of the least desirable approaches since (a) collection efficiencies are poor and vary significantly with physical and chemical properties of the substances being collected; (b) condensation of water with attendant trap plugging and hydrolysis of collected organics can occur; and (c) aerosols (microfog) can form and not be trapped unless electrostatic precipitators are used. If significant amounts of moisture are present, as is often the case with combustion processes, incineration, or absorber vent gases, the trap will contain a two-phase system which will require special handling before analysis. Cryogenic trapping at temperatures sufficient to condense oxygen or nitrogen requires the use of special equipment to carry out analyses.²⁸

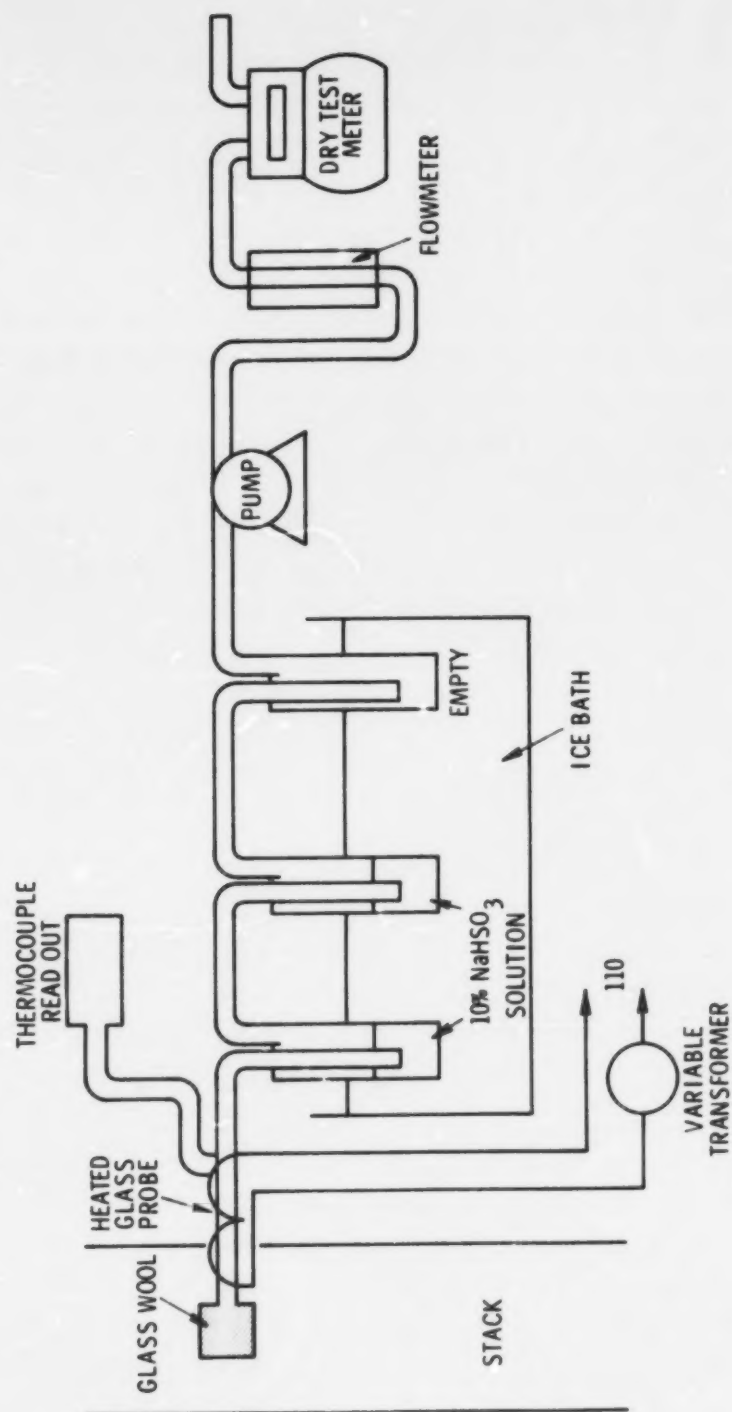


Figure 8. Sampling train for aldehydes

3.1.1.3 Use of Porous Polymer Adsorbents in Sampling Gas Streams

Potentially, the most attractive method for collecting and concentrating organic substances from fugitive or stationary emission sources employs the adsorption and/or partitioning properties of materials normally used in gas chromatographic analysis to retain organic substances selectively while removing the major diluent gases, such as air, nitrogen and water vapor. By proper selection of materials which retain little water, separation of organic substances from water vapor can be accomplished even in samples taken in humid atmospheres. Various types of chromatographic materials have been used. They include charcoal, molecular sieves, liquid phases on solid supports (e.g., Dexil 300 GC on Chromosorb AW HMDS and Silicone oil DC 200 on Chromosorb), and porous polymers.

The retentive characteristics, varied polarity, high-thermal stability, and low affinity for water of porous polymers, suggest that these materials might be the best media for efficiently collecting and enriching organic substances. However, the varied nature of the emission sources requires an evaluation of the limiting properties before specific applications can be defined.

A very simple sampling system using the porous polymer approach is shown in Figure 9. This system is suitable for higher molecular weight hydrocarbon components (C₇ and above). The sampling time can be short -- 5 to 15 minutes at flow rates of 0.075 cfm to collect sufficient material for analysis by GLC/MS using thermal desorption. Typical dry test meters are not very accurate for yielding the total gas volume at such low flow rates.

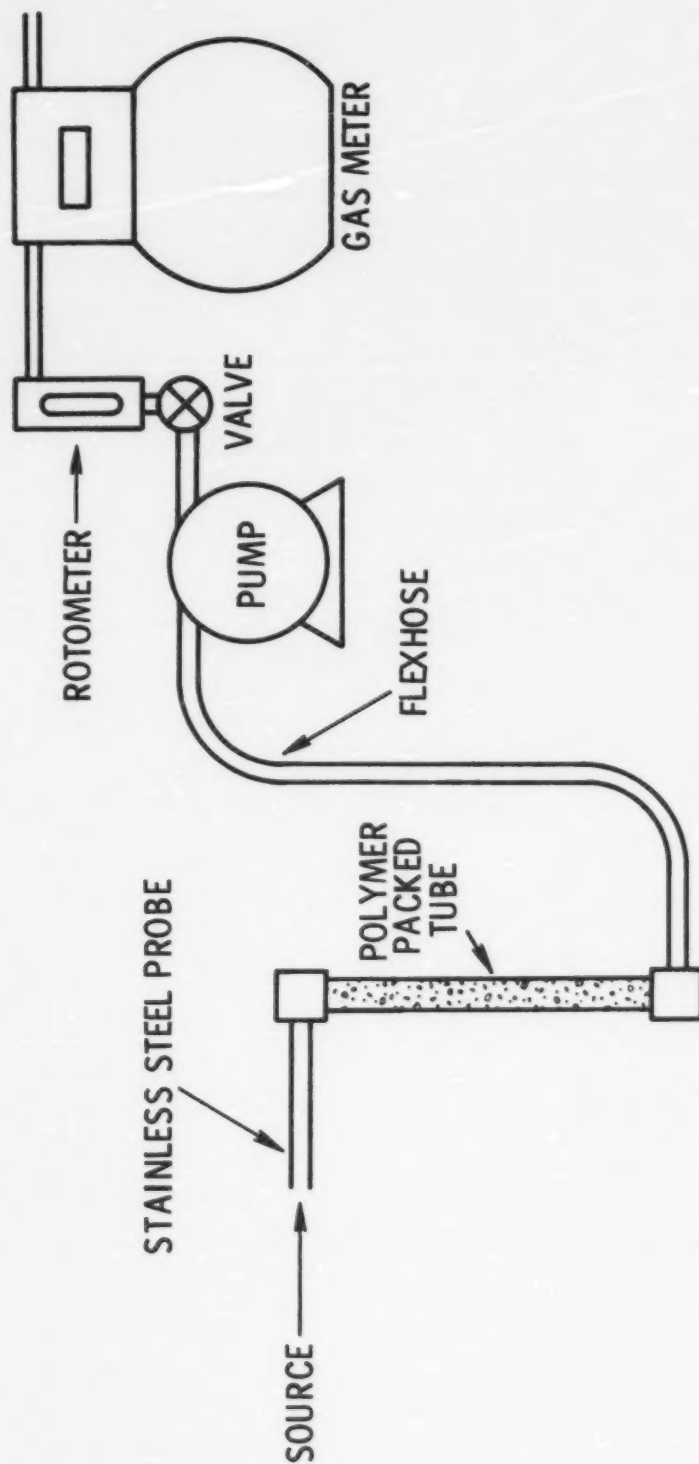


Figure 9. Porous polymer vapor sampling method

The sampling system as shown in this illustration consists of a 1/4 in. or 3/8 in. stainless steel tube 6 in. long packed with porous polymer bead material. This sampling tube is attached to a pump (Model MP-155 Metal Bellows Corp.), a rotameter with valve (Dwyer 0-5 SCFH), and a gas meter (Type AI-110 American Meter Co.). The pump is required because there is an appreciable pressure drop due to the packing in the tube.

A similar train, shown in Figure 10 would replace the pump with an evacuated cylinder to eliminate pump fluctuations in the sample lines. The cylinder used for Freon refrigerant of about 0.023 m³ volume is convenient and should be equipped with a thermocouple or other temperature readout and a vacuum gauge. A glass sampling bulb is used to back-up the polymer packed tube to permit at least qualitative identification of low molecular weight gaseous species. Typical flow rates of 100-200 cc/min for twenty minutes will provide 2 to 4 liters of sampled gas. The temperature and pressure differential in the cylinder before and after collection provides the necessary volume of gas sampled. A partial list of some of the organic materials detected by this procedure from point system and polymer curing ovens is given in Table 3.

Recently Tenax GC, a new, more polar, and more thermally stable porous polymer, has become commercially available. This system is based on 2,6-diphenyl-p-phenylene oxide. Other polymers that have been used in laboratory tests but that are not widely used or are not commercially available, are polyimides, polyamides, polyacrylates, and phosphonated or halogenated resins.

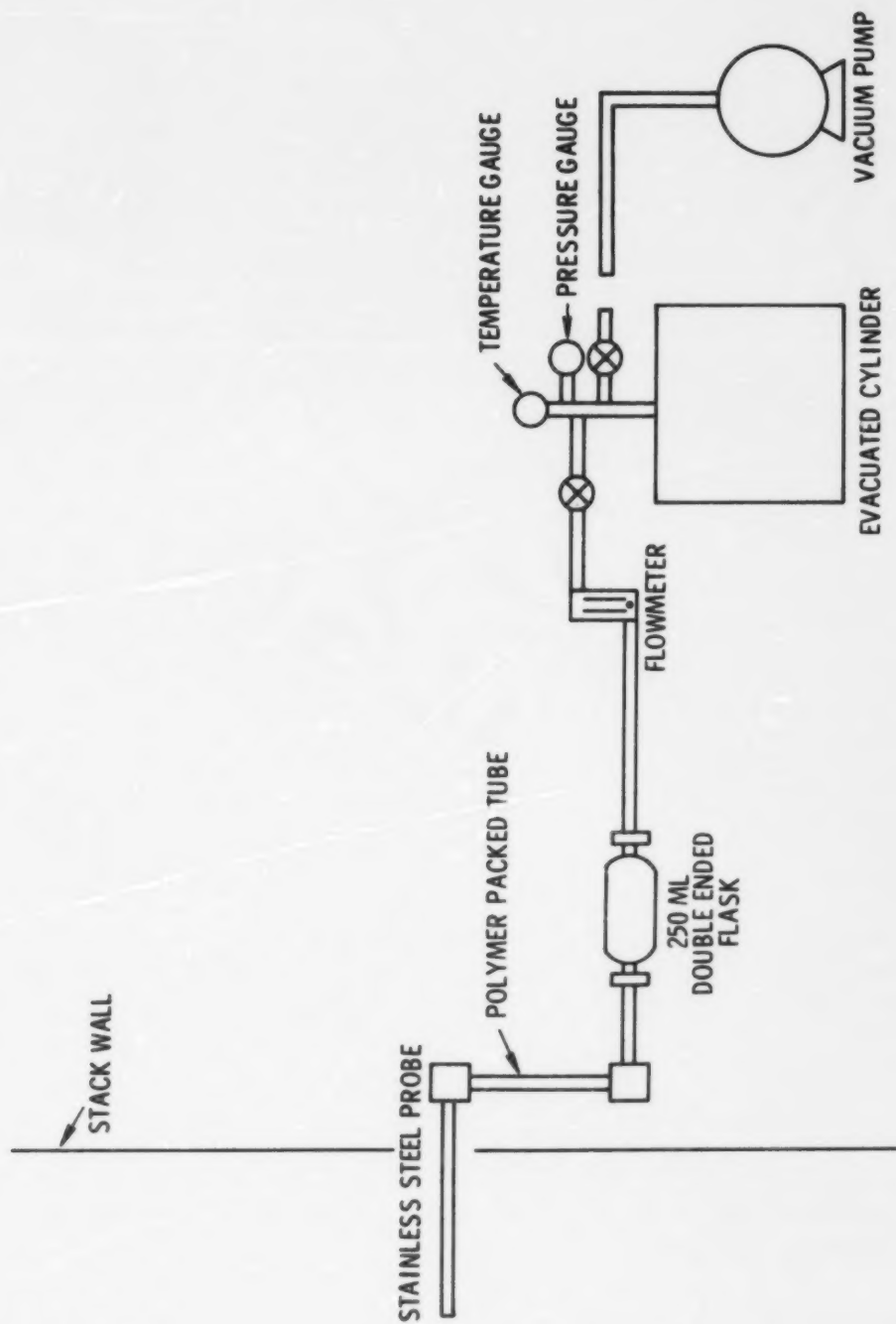


Figure 10. Alternate porous polymer system for organic vapors

Table 3. ORGANIC SUBSTANCES DETECTED FROM PAINT AND POLYMER CURING OVENS BY POROUS POLYMER ADSORPTION AND GC MASS SPECTROMETRIC ANALYSIS

Methanol	2-Ethoxyethylacetate
Ethanol	Chloroform
Isopropanol	Methylene chloride
2-Ethoxyethanol	Cyclohexane
Isobutanol	Dimethylcyclohexane
n-Butanol	Benzene
C ₅ Alcohols	Toluene
n-Propanol	Xylenes
2-Methylbutanol	Styrene
Ethyleneglycol monoethyl ether	Methylstyrene
2-(2-ethoxyethoxy)ethanol	Dimethylstyrene
Formaldehyde	C ₃ Alkylbenzenes
Acetaldehyde	C ₄ Alkylbenzenes
Acrolein	C ₄ Substituted Styrene
Acetone	Trichloroethane
Methylethylketone	Dichloroethylene
Diethylether	Carbon disulfide
Butylacetate	Isopropylbenzene
Saturated Hydrocarbons	Phenol
	Benzaldehyde

Five groups of porous polymers are potentially usable as sorbents for collecting and concentrating organic compounds from stack emissions. These are:

- (1) Porapak series (Waters Assoc., Inc.)
- (2) Chromosorb Century series (Johns-Manville Products Corp.)
- (3) XAD Resins (Rohm and Haas Co.)
- (4) Tenax GC (Enka, N.V., the Netherlands)
- (5) Polyimides

Note: Some XAD-type resins are marketed by Johns-Manville Products Corp. as the Chromosorb Century series; e.g., Chromosorb 102 is XAD-2.

A limited amount of information is available which directly compares the chromatographic properties of these materials. Retention indices obtained under similar operating conditions are reported for two groups, namely, the Porapak, and the Chromosorb Century series.

In general, the retention characteristics of the porous polymers are influenced by both gas-solid and gas-liquid mechanisms. The pore size distribution and micropore volume, the nature of the polymer, and the surface activity all influence the adsorption, diffusion, and partitioning processes. Although specific retention indices are not available for all porous polymers, certain physical property data and a relative ranking of polarity can describe the relative retention characteristics. These data are shown in Table 4.

Table 4. PHYSICAL PROPERTIES OF POROUS POLYMERS

Type	Surface Area (m ² /g)	Ave. Pore Diam. (Å)	Temp. Limit (°C)	Monomer Composition
Porapak P	110	150	250	STY-DVB
Porapak Q	840	75	250	EVB-DVB
Porapak R	780	76	250	Vinyl pyrrolidone
Porapak S	670	76	250	Vinyl pyridine
Porapak N	437	-	190	Vinyl pyrrolidone
Porapak T	450	91	190	Ethyleneglyco- dimethylacrylate
Chromosorb 101	30-40	3000-4000	275 (325)*	STY-DVB
Chromosorb 102	300-400	85	250 (300)*	STY-DVB
Chromosorb 103	15-25	3000-4000	275 (300)*	Cross-linked PS
Chromosorb 104	100-200	600-800	250 (275)*	ACN-DVB
Chromosorb 105	600-700	400-600	250 (275)*	Polyaromatic
Chromosorb 106	-	-	250 (275)*	Cross-linked PS
Chromosorb 107	-	-	250 (275)*	Cross-linked acrylic ester
Chromosorb 108	-	-	250 (275)*	Cross-linked acrylic ester
XAD-1	100	200	200-250	STY-DVB
XAD-2	300	90	200-250	STY-DVB
XAD-4	784	50	200-250	STY-DVB
XAD-7	450	90	200-250	Acrylic Ester
XAD-8	140	235	200-250	Acrylic Ester
XAD-11	69	352	200-250	Amide
Tenax GC	(UNK)			Diphenylphenylene oxide

STY-styrene; DVB-divinylbenzene; PS-polystyrene; ACN-acrylonitrile

*Maximum temperature for short duration

The major problems related to the use of porous polymers as sorbents for collecting organic compounds from industrial emission sources are:

- (1) Displacement of Volatile Compounds - The displacement of volatile organic species by less volatile organic substances is a major problem when using porous polymers. High molecular weight compounds are more readily retained than low molecular weight substances.
- (2) Irreversible Adsorption or Poor Desorption Efficiencies - As derived from the information sources and general commercial literature, the most pertinent data to use for porous polymers as adsorbents relate to the chemical classes that cannot be desorbed from the resins. Generally, the adsorption characteristics of most resins are adequate. However, some chemical classes are irreversibly adsorbed or are desorbed slowly over a relatively long period. In this respect, we are referring to the removal of material from the polymer by application of heat and a carrier gas flow.

The resins and associated chemical classes that will provide potentially poor thermal desorption efficiencies are as follows:

Glycols

- Complete adsorption on Chromosorb 103
- Some tailing on Porapak Z, R, and S. Severe tailing on Porapak QS

Nitriles	- Severe tailing on Chromosorb 103
Nitroparaffins	- Severe tailing on Chromosorb 103
Amines and diamines	- Severe tailing on Chromosorb 101 and 102 Porapak N, P, Q, R, S, T. Some tailing on Porapak QS
Anilines	- Severe tailing on Porapak N, Q, S, T, QS Some tailing on Porapak R
Carboxylic acids	- Complete adsorption on Chromosorb 103 Severe tailing on Porapak S. Some tailing on Chromosorb 102 and Porapak Q
Alcohols	- Some tailing on Porapak N. Branch-chain broadening on Chromosorb 101, 102, 103 and Porapak T

Many of these problems can be eliminated by solvent extraction, and this procedure is generally preferred. The solvent must not react with the porous polymer but must still have sufficient solvent power to remove the materials of interest quantitatively. In addition, the solvent should not interfere with the analysis scheme. For the most part aliphatic hydrocarbons such as pentane or hexane will not react with the Chromosorb or Tenax materials and are easily removed to concentrate the

sample prior to analysis. These materials are generally poor solvents, but continuous extraction procedures (Soxhlet extraction, etc.) minimizes this problem.

- (3) Chemical Reaction of Sorbates with Sorbents and Production of Artifact Species - Porapak Q and Chromosorb 102 were found to react with NO_2 ²⁹ oxygen.³⁰ The reaction with NO_2 yields NO , water and nitrated aromatic rings of the polymer plus the possible increased olefinic unsaturation and/or oxidation of the polymer. Oxygen reacts with the resin above 100°C to depolymerize part of it, producing carbonyl compounds. As a result, the use of this type of polymer for adsorption of organics should be restricted to temperatures of about 60°C or lower.

In general, polystyrene-type materials suffer from oxidation and thermal fragmentation at temperatures above 250°C .

- (4) Change in Sorption Properties of Porous Polymers - The reactions discussed above in (3) undoubtedly influence the sorption properties of porous polymers. The displacement phenomena indicated above in (1) also point out potential problems related to physical adsorption changes at collection temperatures below 140°C , where the physical adsorption mechanism for compound retention predominates with the styrene or divinyl benzene systems.

Also, problems may be experienced when using porous polymers under high-humidity, high-temperature conditions. Although Chromosorb 101, 102, and 103, and Porapaks N, P, Q, QS, R, S, and T are hydrophobic,

and Tenax GC has little affinity for water, some water can be adsorbed on the resins. It has been reported that Porapak Q retains up to 3.4 $\mu\text{g H}_2\text{O/g}$ of polymer at 110°C.³¹

At present it is generally assumed, in a qualitative sense, that the interaction mechanism for adsorbates on porous polymers is a combination of both adsorption and partitioning, especially at higher temperatures. Below the glass transition temperature (T_g), absorption of organic vapors by porous polymers occurs through very complex processes. Amorphous polymers would be expected to adsorb organic vapors to a much greater extent if they were in a rubbery state rather than a glass state. Data suggest that surface adsorption mechanisms should predominate for organic molecules at temperatures below 140°C.

- (5) Retention Capacity of Porous Polymers - Pore size determinations for Porapak P and Q indicate that a large proportion of very small pores exist in these resins, particularly Porapak Q. As a result, a large portion of the " N_2 " surface area reported by the manufacturers may not be available to the more bulky organic molecules. Chromosorb 101 has relatively large pores compared to Porapak P and Q.

Estimates of "available" surface area to organic molecules were made by Gearhart and Burke³² for Chromosorb 102, Porapak P, and Porapak Q. The basis for their estimates was the measurement of free energy changes for molecular probe-adsorbent interactions. By relating these measurements for benzene, cyclohexane, cyclohexene, hexane, hexene,

methylene chloride, and chloroform, estimates of "available" surface area were computed. Chromosorb 101 was used as a norm for comparison since it probably has the greatest available surface area. The reported apparent surface areas for Chromosorb 102, Porapak P, and Porapak Q are 95, 37, and 133 m²/g, respectively. These estimates represent 33.7%, 27.1%, and 20.2% of the manufacturer's reported surface areas.

- (6) Thermal Stability of Sorbent - Thermal stability of the porous polymer sorbent is critical principally from the standpoint of the optimum temperature for desorption. If relatively high molecular weight materials (e.g. MW 140) are to be measured, desorption temperatures as high as 290-300°C may be required. Obviously, lower molecular weight materials will be desorbed at lower temperatures. The choice of sorbent for a particular sorbate will depend in large part on the temperature needed if the organic materials are removed by gas flow and thermal desorption.

3.1.1.4 Adsorption on Chemical Substrates and Silica Gel

Sample collecting and concentration techniques based on adsorption on activated carbon have been used extensively. Activated charcoal has been shown to quantitatively remove an extremely broad range of organic contaminants from air. The National Institute of Occupational Safety and Health (NIOSH) has promulgated a general procedure for sampling and analysis of organics in work place atmosphere.^{33, 34} This procedure is based on adsorption of the organics on activated

charcoal and desorption with carbon disulfide followed by subsequent analysis by gas chromatograph. The current NIOSH procedure for vinyl chloride in in-plant atmospheres employs this method. While the adsorption process is quantitative, the recovery of the collected components is usually incomplete and variable.³⁵ The charcoal may also serve as a catalyst to promote alteration of the sample,^{36,37} and it is extremely subject to adsorption of water vapor, which limits the adsorption capacity and can displace the desired organic components. Desorption by heating requires high temperature (up to 400°C) and is accompanied by chemical changes due to pyrolysis of the organic species and thermally enhanced reactions between the components.

Silica gel has been used for collecting three-carbon and higher molecular weight hydrocarbons. The collection efficiency for lower hydrocarbons, such as ethylene, from air, has been demonstrated to be poor even when trapping at dry ice acetone temperatures.³⁸

3.1.1.5 Sampling in Particulate Laden Streams

The porous polymer materials have also been used in particulate-laden streams as a supplemental collection medium following a filter or cyclone collection device. As mentioned earlier, low flow rate particulate systems have been used for collection of the particulate in the probe and filters and the volatile organics in the impinger liquid. A more efficient procedure is to employ the porous polymer in place of or in addition to the impinger collection and thus eliminate some of the differences mentioned earlier.

One of the early attempts at this approach consisted of a probe, heated filter, ice cooled impinger and a porous polymer trap containing Tenax GC. In general, the results indicated that more organic material was collected by the adsorber than by the impinger collectors.

A modification of this technique uses organic liquids in the impingers that precede the porous polymer adsorber. This procedure is generally unsatisfactory because the organic liquid vapors are trapped in the adsorber. The analysis of the collected species is then complicated by the presence of a large quantity of impinger solvent and a small quantity of other collected organic material.

A more appropriate position for the adsorber would be between the filter used to collect particulate and the impingers. The collected particulate could be both inorganic and organic, depending on the filter temperature and nature of the emission source. The porous polymer adsorber will collect organic vapors, but temperature becomes an important factor. In streams with high water content, water can condense if the temperature of the adsorber is below the dew point temperature of the gas. If the temperature of adsorber is too high, organic material will not be collected or can be driven off. As new stack gas reaches the adsorber, an equilibrium will result and the adsorption of the organic materials could be less than quantitative.

Peter Jones et al of Battelle³⁹ reported the results of an organic sampling study that compared these various systems. Block diagrams of the systems are shown in Figure 11. System 4 collected the most material, even more than system 3 if all impinger, filter, and organic absorber contents were added together. Systems 1 and 2, based on the analysis of

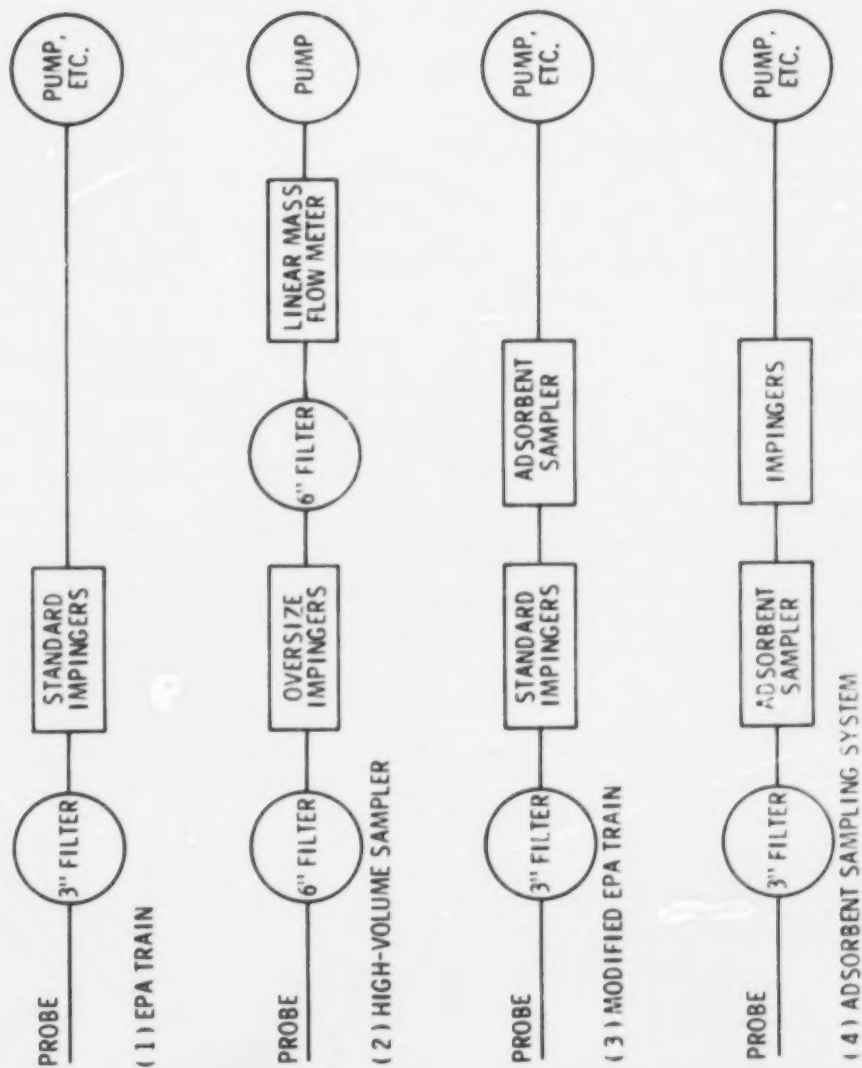


Figure 11. Diagrams of the sampling systems used in the Battelle train evaluation study

organic material collected, were not as efficient as systems 3 and 4. The differences between systems 2 and 4, were apparently caused by the SO_2 content of stack gases. With low SO_2 content, the results were in closer agreement, indicating that "aqueous SO_2 " may chemically alter some of the collected materials.

Based on this work and other recent work, it appears that reasonable results could be obtained using a modified particulate sampling system by placing the porous polymer adsorbent after the filter and before the impinger train.

It should be stressed that this system has been used for materials of relatively high molecular weight and lower volatility than many of the compounds that would be of interest in general organic sampling schemes. At this time, little is known about the accuracy of the techniques since the "true" concentration is not known. It is known, however, which system collects the greater portion of material and it can be assumed that the true value is being approached. In other words there is good knowledge of the precision of particulate sampling, but very little data on the accuracy.

3.1.1.6 Procedures for Low Molecular Weight Materials

The preceding sections of this chapter have dealt with the collection of organic materials using procedures applicable to materials with molecular weight above C_7 , and several procedures have been mentioned for collecting low molecular weight materials. One such procedure was use of a gas sampling bulb after a porous polymer adsorber. Another suggested the use of a Tedlar or Teflon collection bag for an integrated gas sample.

At present, there are many unanswered questions as to the collection efficiency of porous polymers for low molecular weight materials. If water can pass through a Porapak or Tenax adsorber, then there is reason to suspect that methanol, ethanol, and other low molecular weight alcohols may not be collected quantitatively. Fortunately, these materials are not considered highly toxic, and some loss may not be significant.

One possible approach for the collection of low molecular weight materials is to employ a cryogenically-cooled thermal gradient tube patterned after that described by R. E. Kaiser.⁴⁰ The thermal gradient tube will isolate organic emissions that slip through the primary porous polymer sampling tubes.

The sampling train utilizing the porous polymer and Kaiser tubes is shown schematically in Figure 12. An evacuated tank is used as a sampling gas driving force when a positive pressure flow stream is not available. The valve and calibrated flowmeter upstream of the tank adjusts the flow rate in the general region of 100 to 200 cc/minute. Sampling conducted over a 20-minute period provides a total sampled volume of 2 to 4 liters of effluent gas. The cryogenic thermal gradient tubes are fitted with thermocouples, and the porous polymer adsorption tubes are constructed of stainless steel and standard Swagelok fittings. A condensation trap (0°C) is positioned before the polymer tube to trap aerosolized water and water vapor.

Some details of the sampling system includes the following:

- The evacuated cylinder is an 0.02 m^3 (0.83 ft^3) Freon tank fitted with a thermocouple and a 3-in. vacuum gauge to permit calculation of total volume sampled.

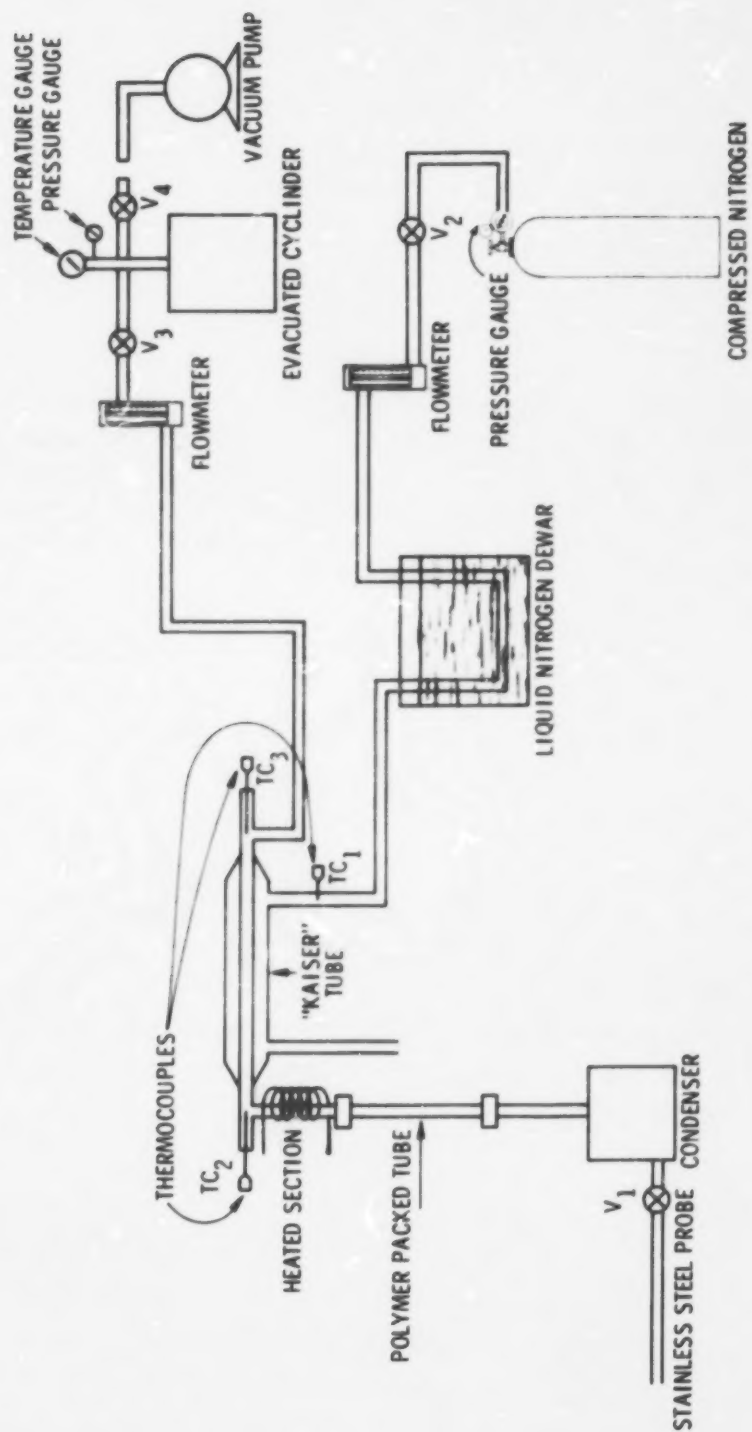


Figure 12. Porous polymer and thermal gradient sampling train

- The liquid nitrogen dewar is a four-liter Nalgene dewar flask (Cat. #4150) constructed of a double wall of highly crosslinked polyethylene.
- The condensation trap is a midget impinger cooled by an ice-salt mixture to about -10°C .
- A photograph of the Kaiser tube is shown in Figure 13. The inner tube of the concentric heat exchanger is a 20-cm length of 3/16 in. stainless steel tubing and the outer tube is a 9-cm length of 5/16 in. stainless steel tubing.
- The porous polymer tube is a 7 inch length of 1/4 in. stainless steel tube fitted with Swage-lok fitting and plugs.

The flow of nitrogen through the jacketed thermogradient tube is adjusted so that the entering nitrogen flow is near liquid nitrogen temperature (-150°C). Under normal operating conditions, the thermocouple designated TC 2 will register about -100°C .

This technique is considerably more complex than desired for field sampling work. However, the method does collect the volatile compounds that may not be collected by the ambient temperature porous polymer sampling system.

3.1.2 Fugitive Emission Methods

In Section 2.1.2 of this manual, procedures were specified for the sampling of particulate and vapor fugitive emissions, which are consistent with the Level I criterion of obtaining large quantities of material in short periods of time. In

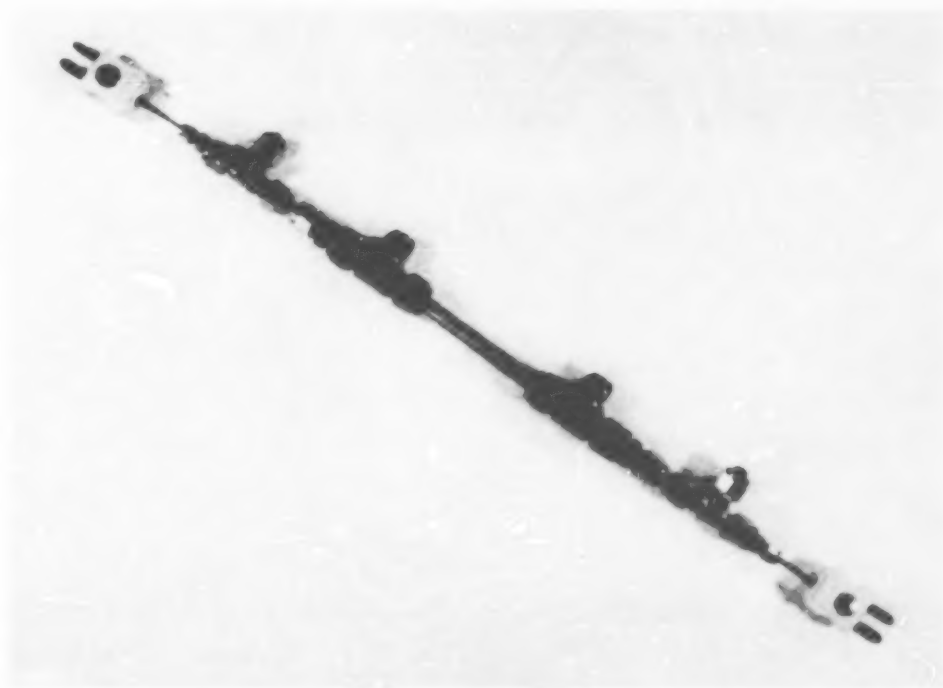


Figure 13. Kaiser tube configuration

a Level II or Level III sampling program, it can be assumed that more effort will be required to obtain the required sample. In the case of particulate sampling for organic materials, the additional time does not change the basic sampling concept of using high volume samplers. However, a more reliable sampling network can be employed. For fugitive vapor sampling, a wide variety of techniques can be employed that are more dependent on the chemical and physical properties of the material to be sampled.

3.1.2.1 Particulate Emissions

For Level I sampling for particulate emissions it was suggested that a one or two high volume samplers collect the emission sample and another sampler collect a background sample. This procedure is suitable if there is little change in the wind direction. In contrast, a network of high volume samplers completely around a source is relatively unaffected by wind direction, but such a network is too complex for even Level II or Level III studies.

In a number of fugitive emission projects, MHC has employed a diffusion model and a five-sampler network that can be used with a Level II or Level III sampling program. Details of this diffusion model are presented in Appendix B.

However, a compromise system of five samplers provides a very satisfactory Level II or III sampling procedure. If four samplers are deployed downwind from a fugitive source as shown in Figure 14, small changes in wind direction during the course of sampling will have little effect on the collection of sample and thus the potential of repositioning the samplers as might be required in the Level I approach is

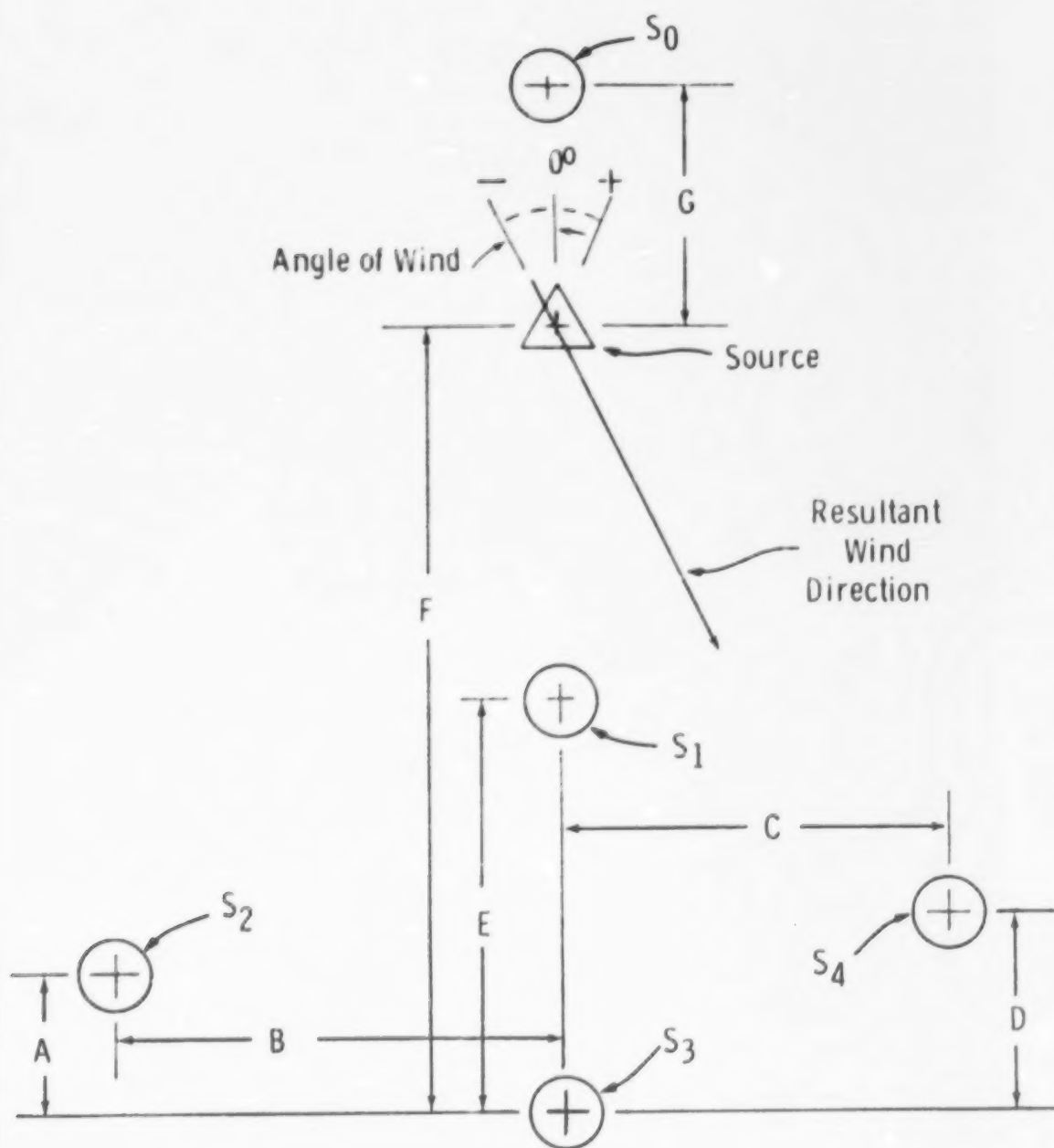


Figure 14. Sampler positions; S₀ - background;
S₁, S₂, S₃, S₄ - sample collectors

avoided. The two samplers that are directly downwind from the source provide some indication of how quickly particulate matter is falling out of air. This provides a simpler system than placing samplers on a tower in order to obtain information on the dispersion of the fugitive emission plume.

The five sampler system requires little more effort than does the Level I system, but does provide for a great deal more flexibility in operation and variation in wind conditions - both direction and velocity.

The roof monitor and quasi-stack procedures described in Level I are equally applicable to Level II or III programs.

3.1.2.2 Organic Vapor Emissions

In the preceding sections several methods are described that can be employed for Level II and Level III fugitive organic vapor emissions. The flame ionization detector chromatograph with suitable separation columns described for stationary source emission is suitable for ambient vapor concentration levels. This sensitivity can be increased by using preconcentration procedures, such as porous polymer tubes, prior to injection into the chromatograph. Organic sulfur compounds should be analyzed on-site with a flame photometric gas chromatograph.

Other techniques such as grab sampling (glass or Tedlar bag) impinger or trapping procedures can be used. A number of procedures have been developed for the in-plant atmosphere study for organic solvents and many of these procedures can be used directly for the sampling of low level fugitive emissions. One source of such methods is the series of procedures

available from the National Technical Information Service, Springfield, Va.⁴¹ At present, there are ten sets with 6 to 16 sampling and analytical procedures in each set. While these methods are generally specific for an individual compound, there is the possibility that a given procedure can be used for many other compounds in the same homologous series.

The other stationary source methods, porous polymer and Kaiser tube collection, can be used in ambient atmospheres by increasing the sampling time.

The high volume sampling systems have also been adapted for vapor sampling. For this purpose the usual 20 x 25 cm filter mat is replaced by a two-stage sampling head. This sampling head contains a 10 cm circular fiber glass filter, followed by a 5 cm x 10 cm vapor trap containing polyurethane foam or coated glass beads. The polyurethane foam has been used successfully for polychlorinated biphenyls⁴², and glass beads coated with cottonseed oil have been used for air-borne pesticide sampling.⁴³ Very recently, it has been observed that many high volume samplers contain a capacitor to reduce sparking, and contamination of samples has been traced to a polychlorinated naphthalene from this electrolytic capacitor. Apparent concentrations of this material were found as high as 1 ng/m³; high enough to prevent determination of pesticides, PCB's and other trace organic materials.

3.2 LIQUID SAMPLING SCHEMES

In aqueous stream sampling, it is imperative that a Level I study be conducted before either a Level II or Level III program is begun. The Level I effort would identify what classes of compounds are of major importance and also provide

approximate levels of this material. It is not the intent of the Level I effort to provide quantitative data, however, from the Level I samples one can determine how much sample will be required for the more specific individual compound identification and quantification. As the analytical procedures to be employed in Level II and Level III studies will generally be rather sensitive, it will not be necessary to collect the large quantities of sample specified in Level I unless additional bio-testing is required. Regardless, sufficient sample must be available to satisfy the analytical separation and detection limits. The volume requirements for the standard analysis of wastewater are presented in Table 5.

In general, Level II and Level III sampling programs will provide more sampling time than a Level I study. As a result, mechanical means of collecting samples are preferred, and a considerable number of suitable commercial samplers are available.

3.2.1 Sampling Systems

A major requirement of a sampling system is that it collect a representative sample. Grab samples provide neither average concentrations nor variations in concentration. The average concentration is best determined by a composite sample collected over periods ranging from hours to weeks. Variations in the composition are determined by individual samples taken at specified intervals. The intervals between the samples must be small enough to show these variations. Another problem with processes that show a wide variation is that the flow rate through the source may also vary. The question that must be answered is whether sampling should be done in relation to time or in proportion to the flow.

Table 5. VOLUME OF SAMPLE REQUIRED FOR DETERMINATION OF THE VARIOUS CONSTITUENTS OF INDUSTRIAL WATER¹⁰

	Volume of Sample, ^a ml	Volume of Sample, ^a ml
PHYSICAL TESTS		
*Color and Odor	100 to 500	
*Corrosivity	flowing sample	
*Electrical conductivity	100	
*pH, electrometric	100	
Radioactivity	100 to 1000	
*Specific gravity	100	
*Temperature	flowing sample	
*Toxicity	1000 to 20 000	
*Turbidity	100 to 1000	
CHEMICAL TESTS		
<i>Dissolved Gases:</i>		
†Ammonia, NH ₃	500	
†Carbon dioxide, free		
CO ₂	200	
†Chlorine, free Cl ₂	200	
†Hydrogen, H ₂	1000	
†Hydrogen sulfide, H ₂ S	500	
†Oxygen, O ₂	500 to 1000	
†Sulfur dioxide, free SO ₂	100	
<i>Miscellaneous:</i>		
Acidity and alkalinity	100	
Bacteria, iron	500	
Bacteria, sulfate-reducing	100	
Biochemical oxygen demand	100 to 500	
Carbon dioxide, total CO ₂ (including CO ₃ ²⁻ , HCO ₃ ⁻ , and free)	200	
Chemical oxygen demand (dichromate)	50 to 100	
Chlorine requirement	2000 to 4000	
Chlorine, total residual Cl ₂ (including OCl ⁻ , HOCl, NH ₂ Cl, NHCl ₂ , and free)	200	
Chloroform - extractable matter	1000	
Detergents	100 to 200	
<i>Miscellaneous:</i>		
Hardness	50 to 100	
Hydrazine	50 to 100	
Microorganisms	100 to 200	
Volatile and filming amines	500 to 1000	
Oily matter	3000 to 5000	
Organic nitrogen	500 to 1000	
Phenolic compounds	800 to 4000	
pH, colorimetric	10 to 20	
Polyphosphates	100 to 200	
Silica	50 to 1000	
Solids, dissolved	100 to 20 000	
Solids, suspended	50 to 1000	
Tannin and lignin	100 to 200	
<i>Cations:</i>		
Aluminum, Al ⁺⁺⁺	100 to 1000	
†Ammonium, NH ₄ ⁺	500	
Antimony, Sb ⁺⁺⁺ to Sb ⁺⁺⁺⁺⁺	100 to 1000	
Arsenic, As ⁺⁺⁺ to As ⁺⁺⁺⁺⁺	100 to 1000	
Barium, Ba ⁺⁺	100 to 1000	
Cadmium, Cd ⁺⁺	100 to 1000	
Calcium, Ca ⁺⁺	100 to 1000	
Chromium, Cr ⁺⁺⁺ to Cr ⁺⁺⁺⁺⁺	100 to 1000	
Copper, Cu ⁺⁺	200 to 4000	
†Iron, Fe ⁺⁺ and Fe ⁺⁺⁺	100 to 1000	
Lead, Pb ⁺⁺	100 to 4000	
Magnesium, Mg ⁺⁺	100 to 1000	
Manganese, Mn ⁺⁺ to Mn ⁺⁺⁺⁺⁺	100 to 1000	
Mercury, Hg ⁺ and Hg ⁺⁺	100 to 1000	
Potassium, K ⁺	100 to 1000	
Nickel, Ni ⁺⁺	100 to 1000	
Silver, Ag ⁺	100 to 1000	
Sodium, Na ⁺	100 to 1000	
Strontium, Sr ⁺⁺	100 to 1000	
Tin, Sn ⁺⁺ and Sn ⁺⁺⁺⁺	100 to 1000	
Zinc, Zn ⁺⁺	100 to 1000	

Table 5 (cont'd.). VOLUME OF SAMPLE REQUIRED FOR DETERMINATION OF THE VARIOUS CONSTITUENTS OF INDUSTRIAL WATER¹⁰

	Volume of Sample, ^a ml
<i>Anions:</i>	
Bicarbonate, HCO_3^-	100 to 200
Bromide, Br^-	100
Carbonate, CO_3^{--}	100 to 200
Chloride, Cl^-	25 to 100
Cyanide, Cn^-	25 to 100
Fluoride, Fl^-	200
Hydroxide, OH^-	50 to 100
Iodide, I^-	100
Nitrate, NO_3^-	10 to 100
Nitrite, NO_2^-	50 to 100
Phosphate, ortho, PO_4^{--} , HPO_4^{--} , H_2PO_4^-	50 to 100
Sulfate, SO_4^{--} , HSO_4^-	100 to 1000
Sulfide, S^{--} , HS^-	100 to 500
Sulfite, SO_3^{--} , HSO_3^-	50 to 100

^a Volumes specified in this table should be considered as a guide for the approximate quantity of sample necessary for the particular analysis. The exact quantity used should be consistent with the volume prescribed in the standard method of analysis, whenever the volume is specified.

* Aliquot may be used for other determinations.

† Samples for unstable constituents must be obtained in separate containers, preserved as prescribed, completely filled and sealed against all exposure.

Since the concentrations of organic materials that may be toxic is relatively low, it is suggested that the best approach is to obtain a composite type of sample of at least 24 hours duration. Several such composites may be required if the concentration of materials is expected to be low. Compositing in the basis of flow would be the most desirable, particularly if higher flow rate can be related to increased production activity.

The choice of an appropriate sampling system for this type of program is not a simple one. In contrast to most of the wastewater sampling, a sampler is required that can be used in a wide variety of conditions and not designed for a particular source. Some of the requirements for a system are as follows:

- (1) The sampler must be portable.
- (2) The sampler should be able to take individual samples, with the option of a composite sample.
- (3) Flow-proportional sampling with time-proportional option.
- (4) The sampler should be refrigerated so that collected samples can be maintained at 4°C.
- (5) The sampler should be designed to prevent contamination of samples either from the sampler or from previously collected samples (sampling lines).
- (6) The unit should be self-contained and operate without connection to an external power source for at least 24 hours. Operation on 115 volt lines should also be possible.

- (7) It is imperative that the sampler can function over a 24 hour period with only intermittent attention after the initial set up.
- (8) The sampler should be versatile enough and provide enough options to make it useful for both organic and other types of sampling programs.
- (9) Sample containers should be of glass or Teflon to prevent contamination of the samples.
- (10) The sampler should be weather-proof to the extent that it could operate under all types of conditions and should be explosion-proof for safety in operation.
- (11) The sampler should be equipped with pumps capable of extracting samples from streams that are up to 20 feet below the sampler location.

There are a number of samplers that are commercially available that can meet most of these criteria. A number of such samplers and their capabilities are listed in Table 6. The information shown is from sales literature and data presented in an EPA report by Harris and Keffer⁴⁴ and as a result may not completely cover all of the available models and manufacturers.

It is of interest to note that Harris and Keffer indicated that in their opinion they have had the best success with the Quality Control CVE unit and a schematic of the sampler is shown in Figure 15. They did not have any of the Manning units or the newer ISCO units. Laboratory examination of

Table 6. SAMPLERS FOR WASTEWATER COLLECTION

Name	Model No.	Composite or Sequential	Sample proportional to: Time	Flow	Refrigerated	Purge Feature	Self-contained	Sample Bottles
Sirco Automatic	NW3-8	sequential	yes	no	add ice	separate lines	no	glass
Quality Control	CVE	composite	external	external	no	yes	yes	glass
Quality Control	CVE-II	composite	yes	external	no	yes	yes (4 days)	glass
Isco	1680	sequential	yes	external	no	yes	yes (1 day)	P.P. or glass
Isco	1580	composite	yes	external	no (ice)	yes	yes (18 hrs.)	glass or PE
Isco	1580R	composite	yes	external	yes	yes	no	glass or PE
Manning	S3000	composite	yes	external	no	yes	yes (120 samples)	glass or P.P.
Manning	S4000	sequential	yes	external	no	yes	yes (120 samples)	P.P.
Sigmamotor	WA-2	composite	yes	no	no	no	no	glass or PE
Sigmamotor	WD-2	composite	yes	no	---	no	yes	glass or PE
Brailsford	EV-1	composite	yes	yes	---	no	yes	glass
Brailsford	DU-1	composite	yes	yes	---	no	yes	glass
Brailsford	EP-1	composite	yes	no	---	no	yes	glass
Hants	33	composite	yes	no	---	no	manual	glass or PE
Sirco	MKU57	composite	yes	yes	---	yes	yes	glass
N-Con	Scout	composite	yes	no	---	yes	yes	glass or PE
N-Con	Surveyor	composite	yes	yes	---	Gravity	no	glass or PE

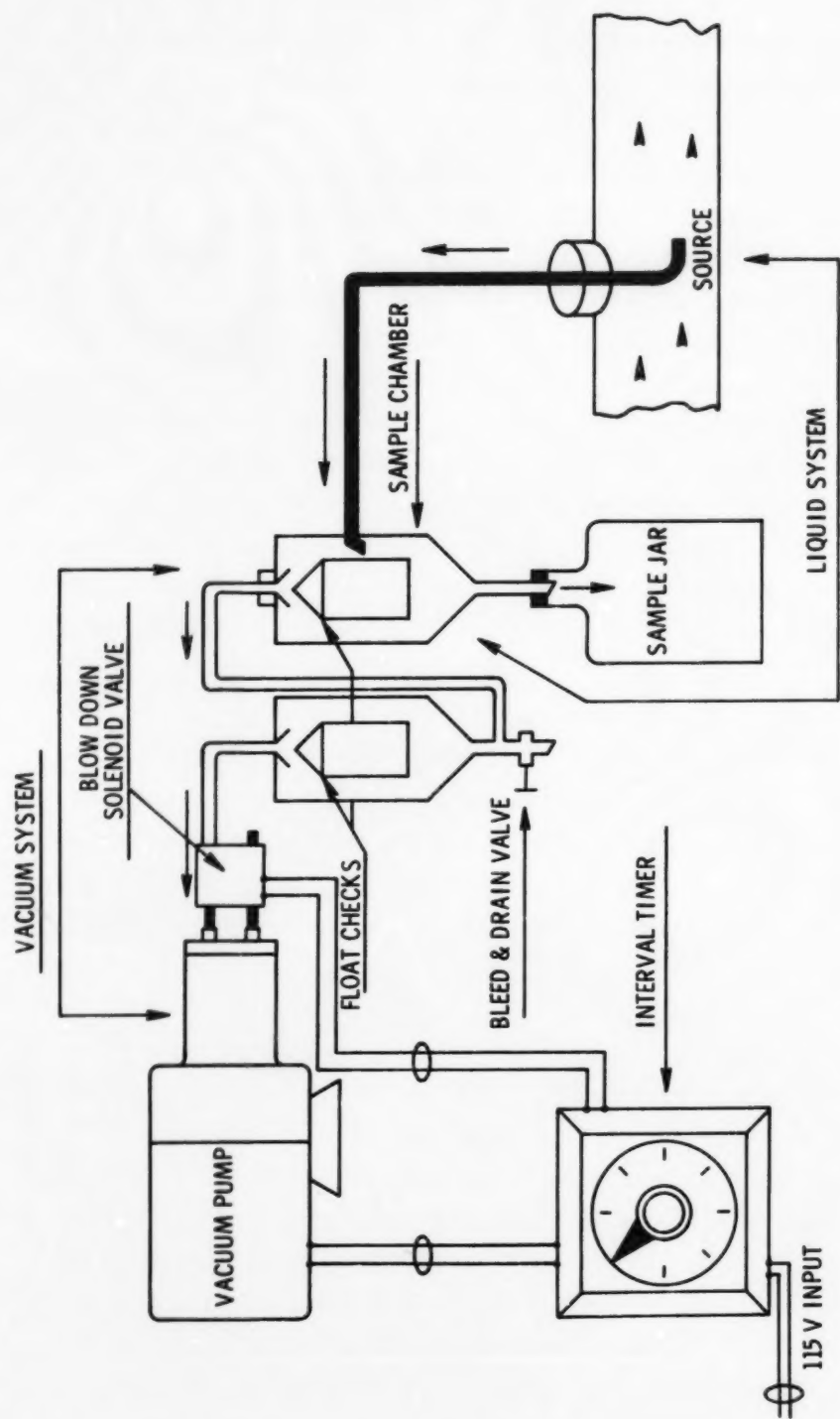


Figure 15. Schematic of the CVE Sampler

the ISCO 1580 and Manning S3000 and S4000 units indicates that these instruments should perform well.

Harris and Keffer⁴⁴ state that the flow compositing of wastewater with appreciable solids content is not justified and further flow-proportional sampling should be restricted to well treated effluents with no visible solids. In this work, the long-term dependability of the sampler is of the utmost importance, and they had the option of choosing a particular sampler for a particular site. For the type of sampling discussed in this manual, a sampler is needed that can be used for short periods over a wide variety of conditions and sites. Therefore, while dependability is important, a sampler should be chosen that has many options and modes of operation and that can be operated to collect many types of samples under a variety of conditions.

The ISCO 1680 or Manning S4000 should provide the necessary capabilities, but these units have not been tested in the field nor have all other possibilities been examined. These two units are sequential samplers. Manual compositing would provide a composite sample if desired. The Manning unit can also be programmed to collect partial bottles. In this way, small composites of a number of individually collected samples can be obtained. For example, samples equivalent to $1/4$ of a bottle could be collected each 15 minutes. Each full bottle would represent a one-hour composite and in 24 hours, 24 one-hour composites would have been collected. Both units can receive sampling signals from an external device and so could be programmed on flow proportion or any other parameter. The Manning sampler employs a vacuum pump, a decided advantage over the peristaltic pump in the ISCO for streams containing high levels of suspended matter. It would appear that glass bottles are not an option to the

standard polypropylene bottles for the Manning unit, a decided disadvantage for organic samples, but they are available for the ISCO sampler. The Manning unit can be ice-cooled, while ISCO has an optional refrigerator available for this sampler. A schematic of the Manning sampler is shown in Figure 16.

It is thus quite clear that each sampler is better suited for certain applications, and the proper selection of a unit must be based on the nature of the sampling program.

Under certain sampling conditions, it would be desirable to employ a concentration-type device in the field. For this approach the CAM in either the high-flow-rate or low-flow-rate versions may be useful. In a Level II or III type of study, some of the disadvantages of the low-flow system would be eliminated since considerably more sampling time would be available.

One possible approach that may be useful is to employ a porous polymer such as Tenax GC in place of the carbon as the organic adsorber. The Tenax has a low affinity for water and if the passage of large quantities of water through the material does not reduce its ability to absorb organic material, it may be possible to directly substitute the Tenax for carbon in the CAM-type adsorber. This type of approach has been employed in laboratory separations of organics from water, so there is evidence that the technique has promise in field sampling. The use of Tenax is an advantage in that generally organics can be removed from this material more readily than from carbon. Also, the technique that will be employed in the handling of the Tenax in gas matrix sampling can be employed on the water-collected samples once the water is removed. The Tenax technique as a field concentrator will require further

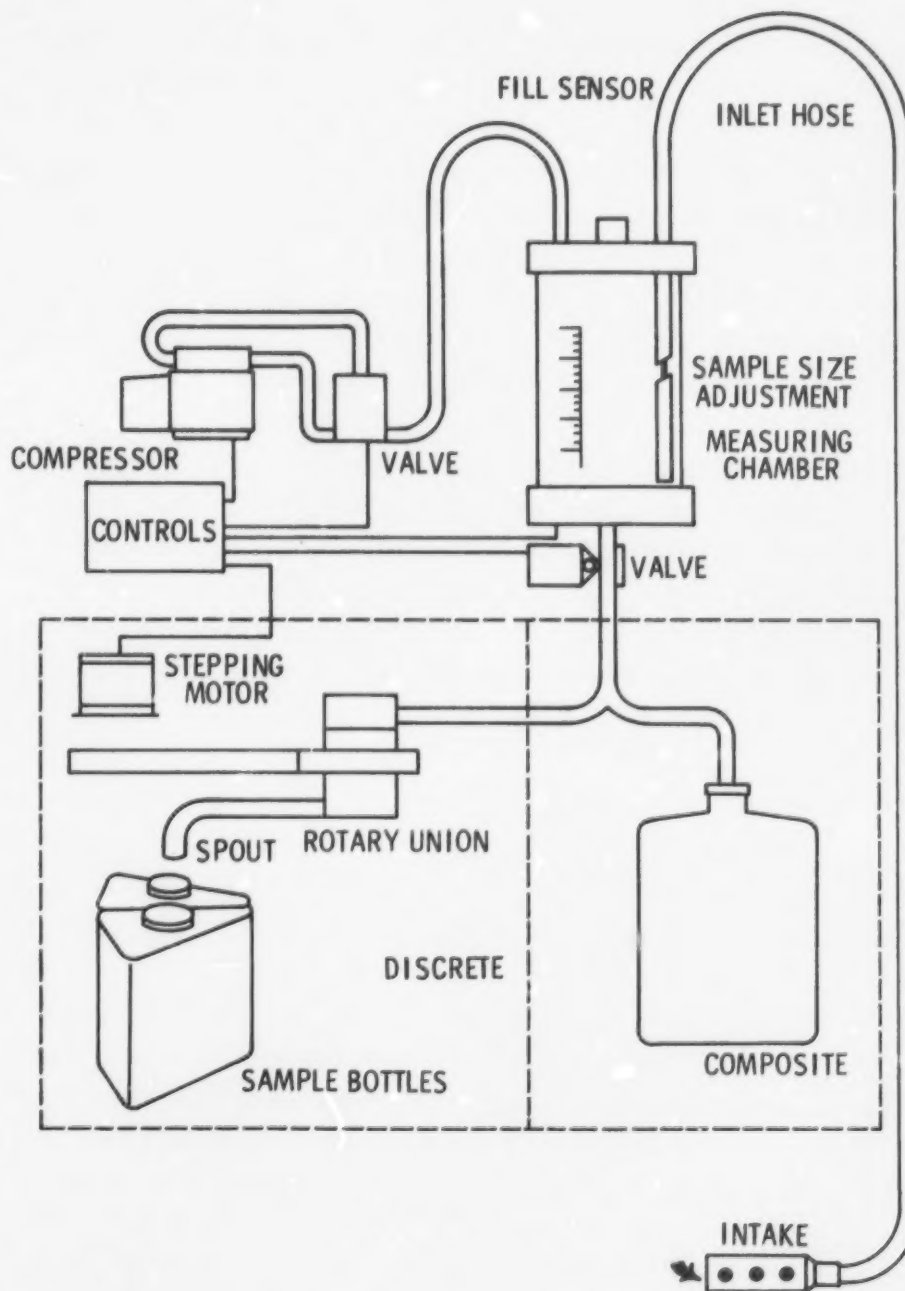


Figure 16. Schematic of the Manning S4000 Sampler

development, and possible loss of low molecular weight volatile organics must be investigated.

3.2.2 Flow Measurement Techniques

The analysis of samples collected in any sampling program at Level II or Level III will provide quantitative data in terms of the concentration in a unit volume. However, in order to assess the seriousness of the emission of a toxic material and relate this to process variables, it is necessary to determine the total flow of a system in a given time. The selection of the proper measurement method will depend on a variety of factors such as cost, accessibility of the source, distances involved, and the characteristics of the stream. In a monitoring program, it is much more feasible to set up a permanent system for measurement of flow rate, but in the assessment type of program, it is necessary to evaluate a trade-off of cost against the reliability of the data.

In an organic sampling program, there are several types of flow that must be considered; flow in open partial-filled channels as in waste streams and flow in completely filled ducts as in process lines or incoming water supplies. In the partially filled stream, the flow can be fairly constant with respect to velocity and depth, or it can be quite varied over a time period. In the closed, completely filled streams, it is usually possible to employ methods that will relate some easily measured parameter such as pressure to the flow rate. Rabosky and Koraído⁴⁵ summarized the methods of flow measurement as listed in Table 7.

Table 7. METHODS OF FLOW MEASUREMENT AND THEIR APPLICATION⁴ 5

Device or Method	Flow Range Measurement	Cost	Ease of Installation*	Accuracy of Data	Application
Mathematical formulas	Small to large	Low	N/A	Fair	Open channels and pipe flow
Water meters	Small to large	Low	Fair	Excellent	Pipe flow
Bucket and stopwatch	Small	Low	N/A	Good	Small pipes with ends or where joints can be disconnected
Pump capacity and operation	Small to large	Low	N/A	Good	Lines where water is being pumped
Floating objects	Small to medium	Low	N/A	Fair	Open channels
Dyes	Small to medium	Low	N/A	Fair to average	Pipe flow and open channels
Salt dilution	Small to medium	Low	N/A	Fair	Pipe flow and open channels
Orifice meter	Small to large	Medium	Fair	Excellent	Pipe flow
Weirs and flow recorders	Small to large	Medium	Difficult	Good to excellent	Open channels
Parshall Flume	Small to large	High	Difficult	Excellent	Open channels
Venturi meter	Small to large	High	Fair	Excellent	Pipe flow
Magnetic flow meter	Small to large	High	Fair	Excellent	Pipe flow
Flow nozzles	Small to large	Medium	Fair	Excellent	Pipe flow
Pitot tube	Small to medium	Medium	Fair	Good	Pipe flow
Rotameter	Small to medium	Medium	Fair	Excellent	Pipe flow

*N/A = Not Applicable

3.2.2.1 Procedures for Closed, Filled Systems

A number of standard methods are available for the measurement of parameters that can be related to flow rate in this type of stream. A summary of these methods and the situations where they can be employed are given in Table 8. Of the methods listed, the water meter and rotameter are restricted to certain types of materials. The venturi meter, flow nozzle, orifice meter, pitot tube and magnetic flow meters are more generally useful, but all require special pipe, pipe sections, or specific pipe designs. As a result, all such devices will require installation during a process interruption. The pressure-sensing devices, with the exception of the pitot tube, will restrict the flow to varying degrees. A high solids content creates problems with all pressure devices. The magnetic flow meter eliminates the flow restriction and solids problems but requires that the liquid be a conductor. Thus it is not appropriate for nonaqueous streams.

Fortunately, the flow rate in many closed-type filled ducts is part of the information required in the control of chemical processes. The required flow rate information can often be obtained from the process logs and instrument data, however, it is essential that the instruments and/or flow devices be recalibrated on or about the time a sampling program is initiated. Arrangements for such recalibration should be made as part of the pretest site survey at the plant location, since scheduling of such recalibration may be a problem and may only be possible during a plant shut-down.

Table 8. METHODS OF MEASUREMENT OF FLOW IN CLOSED PIPES

Method	Parameter Measured	Application	Relationship to flow rate	Remarks
Water Meter	Total flow	fresh water	direct	not suitable of other materials
Venturi Meter	Pressure	most materials	$Q = 0.98AK\sqrt{H}$ (a)	accurate, free of solid accumulation, expensive
Flow Nozzle	Pressure	Waste with moderate solids	$Q = CAK\sqrt{H}$ (b)	between venturi meter and orifice cost and effect of solids
Orifice Meter	Pressure	low solids content	$Q = CAK\sqrt{H}$ (b)	low cost, high pressure loss, not suitable for high solids waste streams
Magnetic flow Meter	Induced Voltage	high solids content	Voltage is proportional to flow	can be used in pipes down to 0.1 inch. Accuracy increases with increased flow. No pressure loss.
Pitot tube	Pressure	straight pipe sections, low solids	depends on configuration	economical in large pipe, solids cause plugging, requires straight pipe 15 to 50 times the diameter.
Rotometers	Flow Rate	clean liquid	direct	suitable for only clean liquids, such as process lines, simple inexpensive, relatively accurate, must be kept clean.

(a) Q = flow rate (ft³/sec), 0.98 coefficient, A = throat area (ft²), $K = \frac{\sqrt{32.2}}{1 - (d_2/d_1)^4}$ where d_2 = throat diameter (ft),

d_1 = dia. of inlet pipe (ft), H = differential head (ft of water)

(b) Q, A, K, H as above, C = coefficient, value depends on design of device

3.2.2.2 Flow Measurements in Open Pipes

The methods that are employed for measurement of flow in open, partially filled pipes range from relatively simple calculations to fairly sophisticated flow sensing procedures that can signal a sampling device. While the first type is suitable for estimating flow for Level I studies, the latter type is required when one is sampling in proportion to the flow rate.

In the simple case of a horizontal or sloped pipe in which the discharge falls into the air, it is possible to calculate the flow rate by the determination of the vertical and horizontal displacement of the liquid after it leaves the pipe (Figure 17). In this case the flow is determined by the relation:

$$Q = \frac{1800AX}{\sqrt{Y}}$$

where

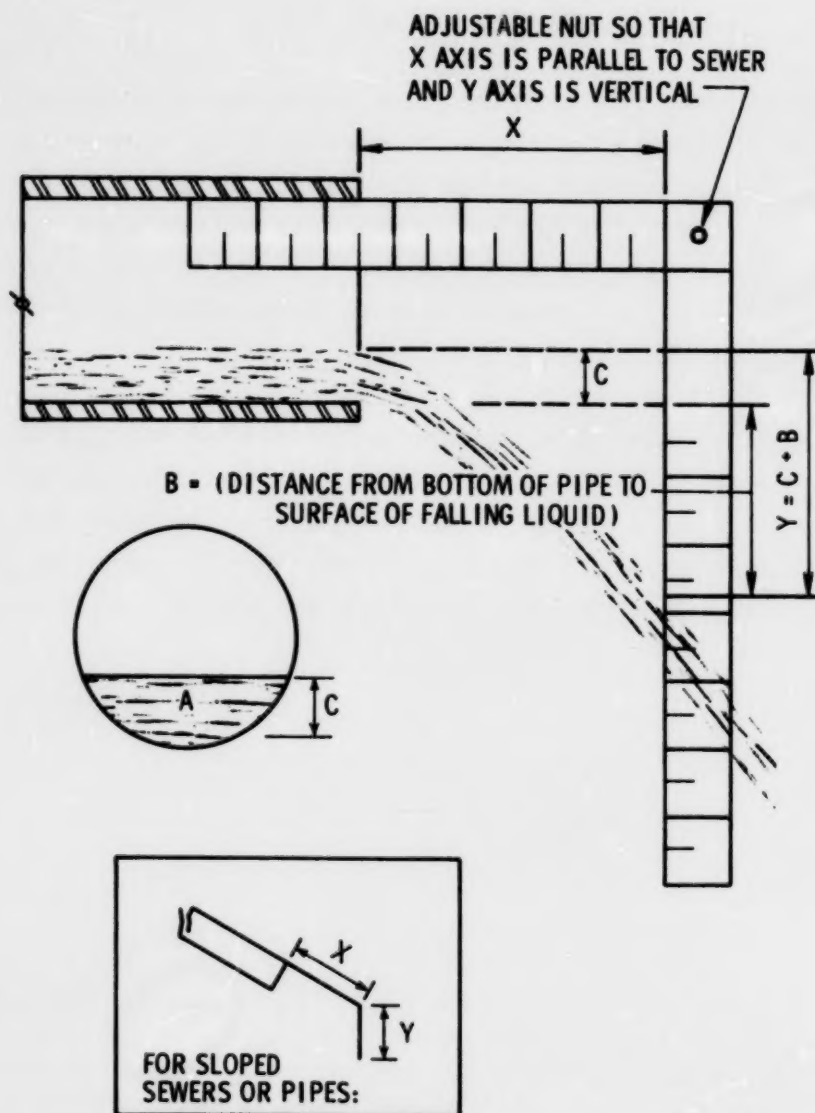
Q = the flow rate (gallons/min)

A = wet cross-section area of the liquid in the pipe (ft²)

X = distance between the end of the pipe and a vertical guage point (ft)

Y = vertical distance from the water surface in the pipe to the intersection of the water surface with the vertical guage (ft)

Another method is called the California pipe method. For this procedure it is necessary to have a horizontal pipe of diameter



OPEN-PIPE FLOW MEASUREMENT - THIS DEVICE, ADJUSTED TO THE SLOPE OF A SEWER AND CALIBRATED, CAN THEN BE CLAMPED TO THE SEWER OUTFALL.

Figure 17. Open pipe flow measurement method⁹

d at least 6 diameters long with free discharge at the open end (Figure 18). The information required is the diameter of the pipe "d" and the distance between the top of the pipe and the level of the liquid "a". The calculation of the flow rate is given by the equation:

$$Q = TW$$

where:

Q = flow rate (gal/min)

$T = 3900 (1-a/a)1.88$

and $W = d^{2.48}$

with both a and d expressed in feet

With this type of measurement, it is possible to employ water level devices to continuously determine the value of "a". In this way changes in the flow rate can be recorded, or the water level device can be employed to operate, through the proper electrical circuits, a flow proportional sampler.

It is also possible to measure flow from the wet cross section area and the average velocity of the liquid because the flow is equal to the area times the average velocity. The average velocity can be measured by pitot tubes and other types of velocity meters. Floating objects can be employed for measuring the surface velocity and by assuming the average velocity of the waste stream is 85% of the surface velocity.

For the most accurate measurements of flow, some type of restricting device such as a weir is constructed across the

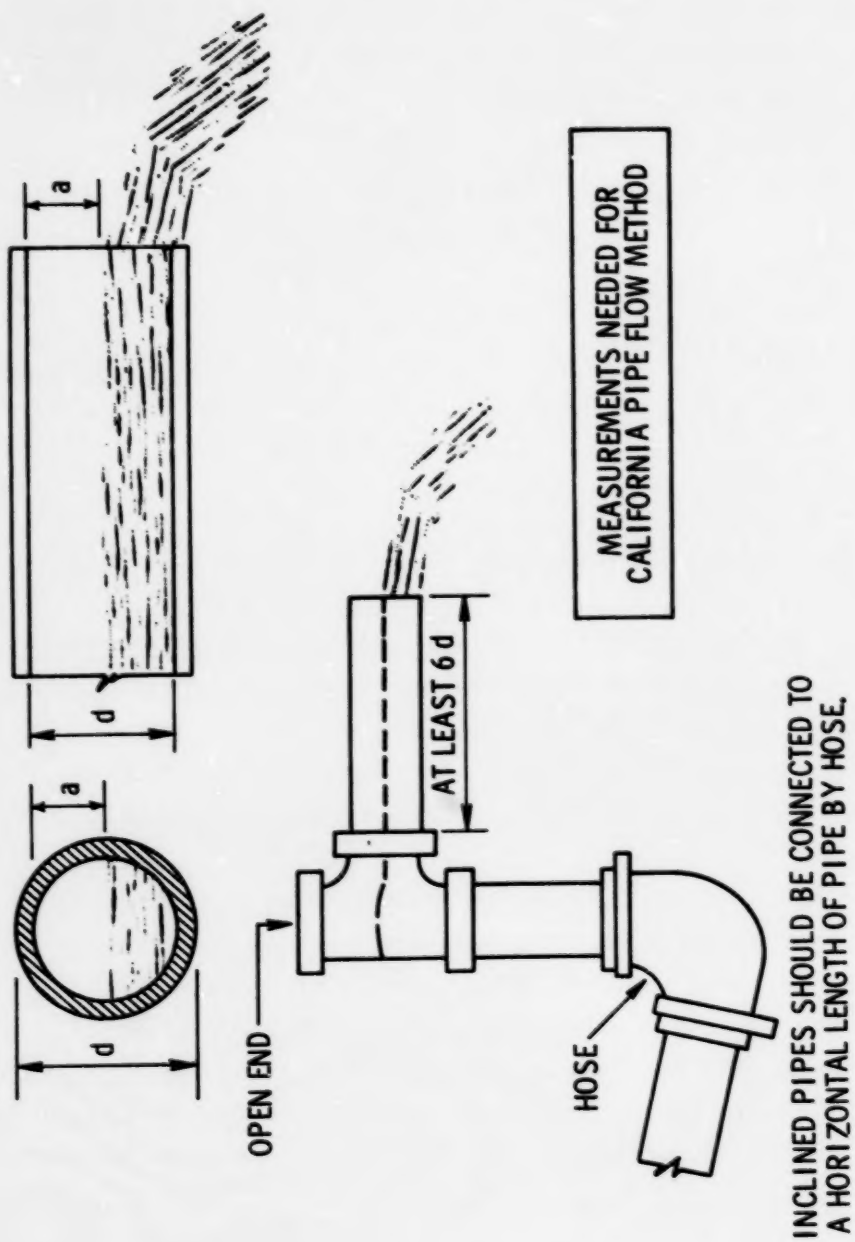


Figure 18. California pipe flow method⁹

pipe so that the liquid flows through a specific size opening and the flow is proportional to the depth of liquid at a given distance upstream from the weir. Most of the devices used for controlling flow-proportional sample require a weir or other such device to be installed in order to maintain a range of depths behind the weir. One major problem with a weir is that solid in the waste stream tends to accumulate behind the weir and can influence the measurements. The device is constructed with a pipe section and thus is considered as a permanent installation. Plastic weirs which can be installed as a temporary device in a half-open pipe have recently become commercially available. Typical weirs are of the 60- or 90-day V-notch or rectangular design, as shown in Figure 19, and the data required for their use in flow measurement is available in most hydraulics handbooks.

One of the most widely used devices for flow measurement is the Parshall flume, a specially shaped channel consisting of a converging section, a throat, and a diverging section, as shown in Figure 20. As with the weir, data are available to relate the head of water above the floor in the converging section to the flow rate. Plastic flumes are available that can be installed in existing pipes. A major advantage of the flume is that it is self-cleaning, and suspended materials do not tend to accumulate behind the flume.

3.2.2.3 Control of Flow Proportional Sampling

Many of the samplers discussed in the sampling section can accept a signal from an external device to permit the collection of flow proportional samples. The signal can be obtained from continuous flow measuring devices that typically are used in conjunction with a weir or flume. Since the

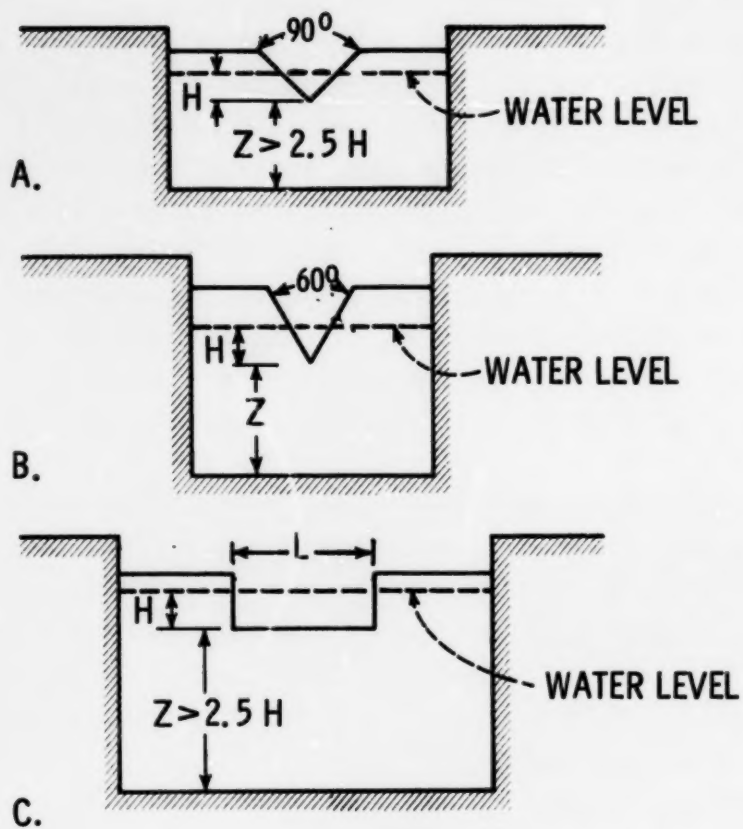


Figure 19. Typical V-notch and Rectangular Weirs¹¹
 (A. $Q = 2.48 H^{2.48}$; B. $Q = 1.43 H^{5/2}$;
 C. $Q = 3.33 L H^{3/2}$)

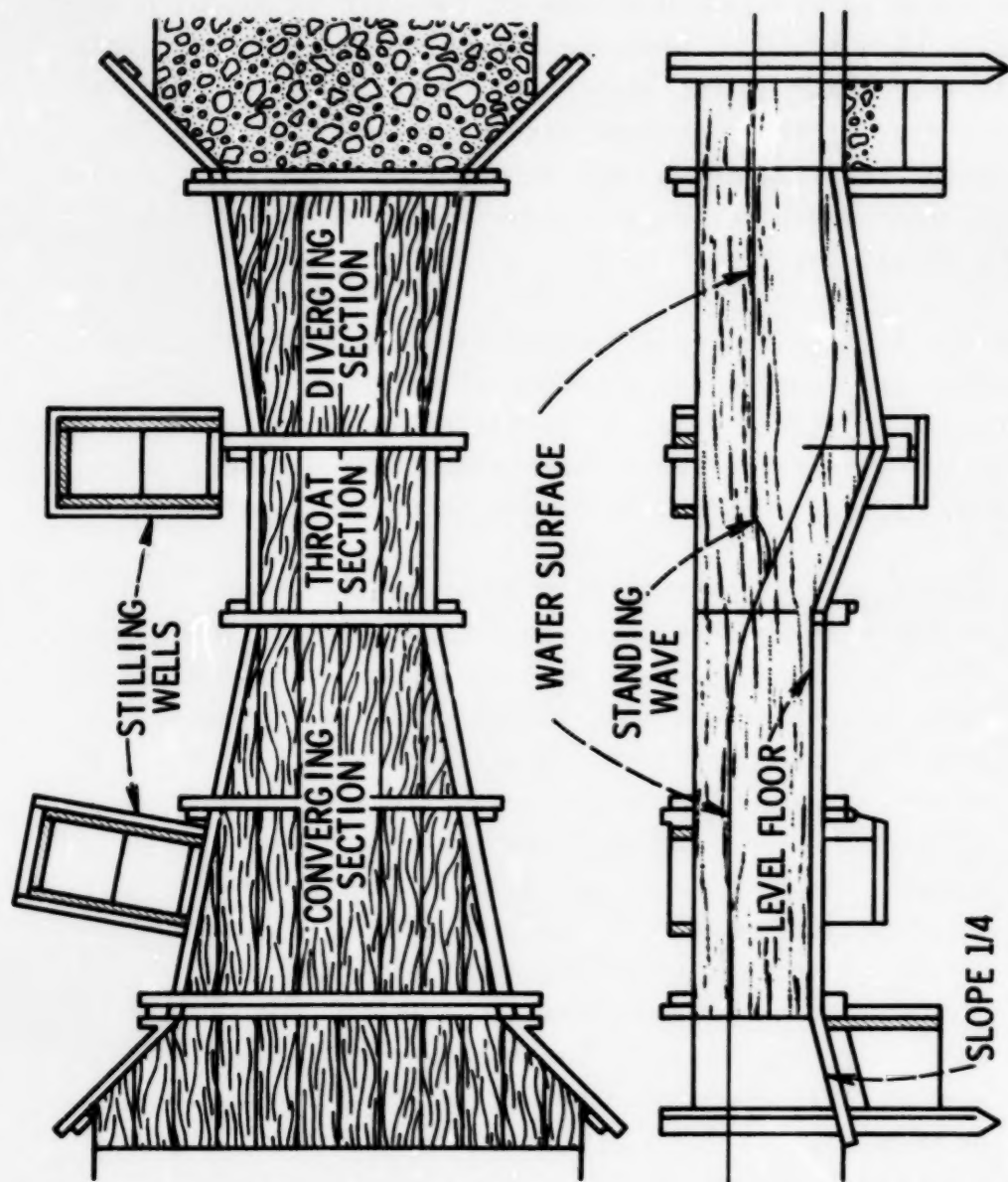


Figure 20. Design of Parshall Flume

water level varies just upstream of the weir or flume, a sensor such as a float or pressure-sensitive device can provide an electrical signal for continuous recording of the liquid depth. Most of these devices have built-in capability for converting the flow depth data into a flow rate, and, in addition, can be set to trigger the sampling device at some preset liquid level.

There are a large number of recording devices commercially available and they employ a number of different methods to determine the liquid level. Details of a number of such devices, using three different approaches, are outlined below, and they represent the types of equipment available.

ISCO Model 1470 - This flow meter senses water levels with a float upstream from a weir or flume which has known flow vs head characteristics, and then integrates the water level with time to measure the passing volume. The float, of the type typically used in a water closet, is available to cover either a six-inch or twelve-inch height range. The Model 1470 employs a specially designed calibration disc for each specific flume or weir shape and this disc must be replaced if the flow meter is used with a different type of weir. If required, the manufacturer will supply special discs for non-standard weirs or flumes or open pipes. The flow meter can be obtained with the required interface to trigger the sampler at a set liquid level.

Fisher and Porter Model 10F1275 - This unit employs a boat-shaped plastic float to sense liquid level. The basic unit is available in

many options and provides only depth information. Conversion to flow is accomplished from tables relating depth to the type of weir or flume.

ISCO Model 1700W - ISCO will soon release this flow meter. It employs a different principle for operation than the Model 1470. In the new model, a tube is placed in the liquid upstream from the flume or weir and air is bubbled slowly through the tube. The flow meter senses the pressure required to maintain the bubbling and relates this pressure to the liquid depth. In contrast to the machined disc used with the Model 1470, the Model 1700W employs a transparent plastic disc with darkened areas and a photocell arrangement to convert the depth to flow rate. A separate plastic disc is required for each type of weir or flume, however, the discs are easily changed for a new flow situation. Although this device has not been field tested as yet, the prototype demonstrated seemed to operate reliably. This device can be employed to trigger a sampler at a preset liquid level.

Manning F-3000 Series - The Manning Dipper Flowmeter has many features that indicate it would be very useful in a source assessment type of program. The unit is relatively small and can be set up by one man in about 10 minutes. The flow meter works on a dipper principle and, with an internal switch, can be used for obtaining flow in round pipes, flumes or weirs (and other types of channels on request). The dipper

measures the liquid level by sensing the surface of the liquid and does not enter the liquid. A thin non-corrosive probe is lowered on a wire controlled by a motor. When the probe makes contact with the surface, a micro-ampere circuit is completed through a conductive liquid to a ground return. The signal reverses the motor, raising the probe above the surface. After 5 seconds, the probe is lowered, contacts the surface and reacts again. The changes in the cable length during this dipping action are translated into rotation of a measuring wheel and hence to an electronic servo system.

The flow-proportional output from the servo system can be used to record flow on a chart and provides an input to a totalizing circuit. In order to obtain the actual flow rate, it is necessary to multiply the reading over a time period from the totalizing circuit by the maximum flow/minute of the system. While the system does not give the total flow directly, it is a simple matter to obtain this data. The unit is battery powered and can supply flow data for a period up to 7 days on a chart powered by a spring-driven 8-day clock. The flow meter includes capability of controlling an automatic sampler on a flow proportional basis.

As indicated earlier, sequential or composite sampling can be done on either a time basis or flow proportional basis. Time-based samples can give a distorted picture, overemphasizing

the nighttime readings when low flow and processing activity occurs and underemphasizing the higher flow and processing of the daylight hours. This is not critical in around-the-clock processing situations, however, most industries show considerable variation in daily activity. The flow-measuring devices described have a sensor that can activate a sampler when the effluent stream reaches a predetermined level.

In general, there are two methods that are employed for taking the sample, the time constant-volume variable method (TcVv), and the time variable-volume constant method (TvVc). Many samplers can operate on either principle, however, the TvVc method provides the same quantity of liquid each time and thus eliminates the possibility of collected samples that are too small for analysis during low flow periods. This is especially important in sequential sampling. In operation, the TvVc method provides for shorter intervals between samples during periods of high flow (and possible high process activity) and thus may detect occasional non-periodic discharge of materials that may not be detected on a TcVv basis.

3.2.3 Preservation of Samples

Once the sample is collected, it is essential that it be maintained for storage and shipment in such a way that it is representative of the stream to be investigated. Complete and unequivocal preservation of samples is a practical impossibility because complete stability of each and every compound can never be achieved. The preservation techniques are intended to retard chemical and biological changes prior to analysis.

Some of the potential pitfalls in handling the samples include:

- (1) Breaking of glass containers during handling and shipment
- (2) Improper cleaning of glass containers
- (3) Use of cap liners other than Teflon (this material eliminates plasticizer or adhesive contamination)
- (4) Biological degradation
- (5) Loss of metals and other materials to the container walls
- (6) Possibility of expansion if frozen and breakage of the container
- (7) Potential loss of low molecular compounds if head space in container is not minimized
- (8) Chemical changes in components due to time delays between sampling and analysis

For this program, our major interest is the organic constituents in the sample. However, as has been noted many times, it would be desirable to obtain a sample for other analyses as well. In order to provide an understanding of the complexity of the problem, recommended sample preservation and maximum holding period data are given in Table 9 for a variety of measured parameters.⁴⁶ This list includes many of the parameters that are typically measured to characterize waste water samples. It is obvious that a wide variety of preservation methods are employed.

Table 9. SAMPLE PRESERVATION AND MAXIMUM HOLDING PERIODS⁹

Parameter	Preservative	Maximum Holding Period
Acidity-Alkalinity	Refrigeration at 4°C	24 hours
Biochemical Oxygen Demand	Refrigeration at 4°C	6 hours
Calcium	None required	7 days
Chemical Oxygen Demand	2 ml H ₂ SO ₄ per liter	7 days
Chloride	None required	7 days
Color	Refrigeration at 4°C	24 hours
Cyanide	NaOH to pH 10	24 hours
Dissolved Oxygen	Determine on-site	No holding
Fluoride	None required	7 days
Hardness	None required	7 days
Metals, Total	5 ml HNO ₃ per liter	6 months
Metals, Dissolved	Filtrate: 3 ml I:I HNO ₃ per liter	6 months
Nitrogen, Ammonia	40 mg HgCl ₂ per liter - 4°C	7 days
Nitrogen, Kjeldahl	40 mg HgCl ₂ per liter - 4°C	Unstable
Nitrogen, Nitrate-Nitrite	40 mg HgCl ₂ per liter - 4°C	7 days
Oil and Grease	2 ml H ₂ SO ₄ per liter - 4°C	24 days
Organic Carbon	2 ml H ₂ SO ₄ per liter (pH 2)	7 days
pH	Determine on-site	No holding
Phenolics	1.0 g CuSO ₄ /l + H ₃ PO ₄ to pH 4.0 - 4°C	24 hours
Phosphorous	40 mg HgCl ₂ per liter - 4°C	7 days
Solids	None available	7 days
Specific Conductance	None required	7 days
Sulfate	Refrigeration at 4°C	7 days
Sulfide	2 ml Zn acetate per liter	7 days
Threshold Odor	Refrigeration at 4°C	7 days
Turbidity	None available	7 days

In general, the preservation methods can be summarized into four types: (1) use of HgCl_2 to prevent bacterial action; (2) use of acid (either HNO_3 or H_2SO_4) to prevent bacterial action, form soluble salts, or to form complexes; (3) use of alkali to form salts of volatile compound; and (4) refrigeration to prevent bacterial action, to retard chemical reactions, and to reduce loss of volatile compounds.

For the purpose of this study and the possibility that other analyses will be done on the collected sample, it is suggested that preservation at 4°C is the best compromise. It should be noted, however, that this is not the preferred method for samples to be analyzed for trace metal content. In addition, filtering the sampling presents an additional problem. It is generally recommended that samples for organic analysis not be filtered because the organics are frequently adsorbed on the surface of the suspended particles. Instead, filtering on-site followed by stabilization of the filtrate with HNO_3 is suggested for trace metal analysis. This will present a major problem if analysis for both types of materials is desired, especially for Level II or Level III programs. At this time there is no obvious solution to the problem. However, since the major interest in this manual is organic materials, the refrigeration method is suggested and the loss of some metal compounds must be accepted.

3.3 SOLID SAMPLING PROCEDURES

In the Level I approach to solid sampling, the specified techniques were basically "grab" samples taken from convenient locations or employed existing sampling devices if they were available from the plant quality assurance programs. There was no attempt to install sampling devices since these

installations would not fall within the Level I cost and manpower structure.

For the Level II and Level III program there is increased emphasis on the acquisition of a representative sample in order to identify specific organic compounds and to relate these compounds to the process conditions. In this context, some of the available types of mechanical samplers can be employed to obtain the samples. If the analysis information is essential to the program, the installation of these devices can be justified.

As indicated in the Section 2.3 on Level I sampling, many of the procedures are available from the ASTM methods. All of the references listed in the Level I section are appropriate for the higher level studies.

3.3.1 Sampling of Bulk Material

The methodology for Level II and III sampling is basically identical to that employed at Level I. The only difference is that more sampling locations within the source are essential to establish a pattern of variation and trends in the composition of the material. Along with the larger sample, mechanical methods of compositing and reducing sampling size would be employed instead of alternate shovel and cone and quartering techniques. ASTM procedure D2013-72 "Preparing Coal Sampling for Analysis"²² describes a sample divider (riffle) and several rotating devices to permit sample reduction. Diagrams of these devices, indicating the principles of operation, are shown in that procedure. These types of devices generally eliminate the bias in sample size experienced in the alternate shovel and cone and quartering techniques.

The objective of a Level III study is to evaluate the effect of process variables on the emissions and composition of material. This will require that sampling must be performed on the process material to establish the degree of variability to be expected under "normal" operating conditions. Unless the degree of variability is known, it would be impossible to establish if the process variables were causing a change in the material composition. There is no question as to the ability of the analytical methods to measure small variations in composition. Therefore, it is essential that the sampling should be done in a manner that such variations represent process changes rather than sampling anomalies. A number of individual samples should be obtained and analyzed separately to provide both an average value and the variability of the composition instead of trying to obtain an "average" sample.

3.3.2 Sampling From Moving Streams

The Level I approach for moving streams was based on the "stop belt" grab sampling procedure. This procedure could equally apply to Level II and III studies within the restrictions of grab sampling techniques. As in bulk sampling, additional individual samples would be desirable and these samples should be subdivided by riffles or other devices to obtain a single sample for analysis.

Level II and Level III programs also present the possibility of installing mechanical devices such as a ram, rotating cutter or slip streams to provide periodic samples. These devices must be designed for the specific site. As a result, the device and its design must be discussed in detail with plant management personnel.

The ram or straight line sampler will provide the most accurate sample. The design is such that entire cross-sections of the material in the stream is removed each time the sampler operates and an equal time is spent in each portion of the stream. In general, the sampler operates at right angles to the stream, although some of these devices operate at an angle to minimize disturbing the sample and thus reduce the amount of segregation that can take place.

SECTION IV

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APPENDIX A

GENERAL INFORMATION

The purpose of the manual is to present sampling procedures that can be employed in the collection of samples of organic material in gas, liquid or solid process streams and emission sources.

A.1 PRELIMINARY CONSIDERATIONS

The success of any sampling mission depends upon the effort spent in obtaining in-depth background information on the processes involved and in a comprehensive preliminary survey. Table 1 lists some of the industrial processes which could serve as point sources of organic emissions.¹ The emission characteristics are presented in terms of composition, humidity, acid content, temperature, pressure, and flow rate. While this table presents only a cursory view of the emission sources, it can serve as a frame of reference for identification of potential problem areas prior to the preliminary survey. Sources that have reactive emissions (NO_x , SO_2 , acids, oxidizing atmospheres), elevated temperatures, and high water loadings would have to be approached with caution to assure that the final analysis were truly indicative of the emission composition.

Table A-1. CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES

Potential Organic Emission Sources	Composition					Humidity, (% RH)	Acid Content	Temperature, °F	Pressure, PSIA	Flow Rate, SCFM
	Part. No.	H ₂	SO ₂	CO	H ₂ C					
Storage Tanks										
		X				0-20	X	-54 - 300	0-2	<100
Unloading Facilities										
		X				0-20	X	-54 - 200	0-2	<100
Chemical Reactors										
Non-Catalytic										
		X				0-20	X	-20 - 1000	0-1500	100-10,000
Catalytic										
Fluidized Bed		X				0-20	X	0 - 300	0-50	100-10,000
Fixed Bed		X				0-20	X	0 - 300	0-50	100-10,000
Moving Bed		X				0-20	X	0 - 300	0-50	100-10,000
Distillation Column										
		X				0-98	X	80 - 250	0-50	100-10,000
Flash Separator										
		X				0-98	X	-48 - 300	0-50	100-10,000
Filters										
Pressure Leaf Filters		X				0-98	X	70 - 150	0-10	100-10,000
Rotary Vacuum Filters		X				0-98	X	70 - 150	0-20	100-10,000
Mutsche Filters		X				0-98	X	70 - 150	0-10	100-10,000
Horizontal Plate Filters		X				0-98	X	70 - 150	0-10	100-10,000
Tubular Filters		X				0-98	X	70 - 150	0-10	100-10,000
Bag Filters		X	X	X	X	0-98	X	70 - 150	0-10	100-10,000
Mixers										
		X				0-20		32 - 90	0-2	100-10,000
Grinders										
		X				0-20		32 - 90	0-2	100-10,000
Crushers										
		X				0-20		32 - 90	0-2	100-10,000
Scrubbers										
		X	X	X	X	80-95	X	60 - 150	0-10	>10,000
Dryers										
Counter-Current Dryer		X	X	X	X	0-95	X	100 - 300	0-20	100-10,000
Rotary Drum Dryer		X	X	X	X	0-95	X	100 - 300	0-20	100-10,000
Vacuum Rotary Dryer		X	X	X	X	0-95	X	100 - 300	0-35	100-10,000
Spray Dryers										
		X				0-95	X	100 - 300	0-20	100-10,000
Screeners										
		X				0-20		32 - 100	0-2	100-10,000
Vacuum Jets										
		X	X	X	X	95-99	X	270 - 390	25-200	>10,000

Table A-1 (Cont'd). CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES

Potential Organic Emission Sources	Composition					Humidity (% RH)	Acid Content	Temperature, °F	Pressure, psig	Flow Rate, scfm
	Part.	NO _x	SO _x	CO	HC					
Waste Incinerators	X	X	X	X	X	40-95	X	500 - 1500	0-5	>10,000
Utility Boilers	X	X	X	X	X	40-95		500 - 1500	0-5	>10,000
Pneumatic Conveyors	X				X	10-30	X	40 - 90	0-20	>10,000
Conveyor Belts	X				X	0-20		32 - 90	0-2	<100
Extruders		X	X	X	X	0-20		100 - 350	0-2	<100
Pelletizers					X	0-20		100 - 200	0-2	<100
Paint Spray Booths	X				X	0-20		60 - 100	0-5	>10,000
Ovens	X	X	X	X	X	0-50		500 - 1500	0-2	>10,000
Blenders	X				X	0-20		32 - 90	0-2	100-10,000
Cyclones	X				X	0-20		70 - 150	0-20	10,000
Extraction Towers					X	0-90	X	70 - 300	0-50	100-10,000
Piases	X	X	X	X	X	40-95		1500 - 3000	0-2	>10,000
Baggers	X				X	0-20		100 - 200	0-2	<100
Loading Facilities	X				X	0-20	X	-54 - 300	0-2	<100
Cooling Towers					X	40-95		32 - 100	0-2	100-10,000
Settling Ponds					X	40-95	X	32 - 80	0-2	100-10,000
Evaporators					X	0-95	X	100 - 200	0-50	100-10,000
Leaching Vat					X	0-95	X	100 - 200	0-2	100-10,000
Cookers	X	X	X	X	X	0-95	X	100 - 300	0-2	100-10,000
Refrigeration Machines						0-10		-50 - 32	50-300	<100

A.1.1 Preliminary Background Search

The first phase of a sampling mission consists of an in-depth gathering of information relevant to the industry to be sampled. Information is sought which describes the processes in operation in the industry, the nature of the chemical reactions occurring, whether or not the process has been previously determined as a source of vapor, particulate solid, or liquid emissions, and the likely emission characteristics (i.e., information analogous to that presented in Table 1). Any sampling history of similar industries is important and can shed light upon troublesome emission sources. Only after such a literature search should the sampling group elect to conduct a preliminary survey; in addition, it is strongly recommended that individuals thoroughly familiar with the background material and sampling requirements conduct the survey.

A.1.2 Preliminary Survey

Included in the end of Appendix A is a preliminary survey form which shows the type of information to be gathered on the survey.² In the majority of cases it is expected that a visit to the location will be necessary. While this form has been used mainly for stationary source sampling, it includes much of the information required for multi-media sampling program, and so data suitable for water and solid sampling have been added. The type of information required can be summarized as follows:

I. General Data.....basic information on the source, including the nature of expected pollutants and the process from which they are emitted.

II. Detailed Description.....concerning the process, including the raw materials and fuels. Effects of external conditions such as weather and operating schedules are also noted.

III. Sampling Site.....detailed description of the location of the site and the geometries which will concern the sampling crew.* Different data are required if the emphasis is on stack sampling (vapor and particulate), as opposed to liquid sampling or solid sampling. Note that some preliminary measurements may be necessary if they are not already available from the source, particularly on the water content of gas streams and the flow parameters of gas and liquid streams. The recommended methods of sampling are to be included as are the listings of specific raw materials and products which may have to be collected to complete the evaluation of the source.

IV. Safety Checklist.....an itemization of needed equipment and where it is to be obtained. This includes specific equipment needed to set up the test site for sampling. Of equal importance is the determination of the needs of personnel safety equipment so that the sampling team can conduct the program without exposure to toxic chemicals or undue physical risk.

V. Plant Entry.....details specific instructions for accomplishing the sampling tasks with minimum friction between sampling and plant personnel. Plant requirements may include needs for special insurance coverage, special clothing and shoes, or instructions in safety rules at that location. The

*The choice of the sampling site will depend on the nature of the study to be conducted and the end use of the data generated by the study.

inter-corporate agreement section should detail any confidentiality or special clauses that have been negotiated with regard to testing schedules or data control. It has been our experience that considerable time is often required to obtain the cooperation of the plant management in source evaluation programs. Since many of the compounds of potential interest are very toxic, some management officials feel that they have nothing to gain and much to lose if the evaluation study is conducted. It should be stressed to management that the plant being studied has the opportunity to obtain valuable information long before it is required by compliance programs and thus time can be gained for the development of control strategies.

VI. Sample Handling.....itemizes the methods and the location of facilities in which the samples can be processed before shipping or other transfer.

VII. Level of Effort.....presents the costs to management regarding the sampling mission.

VIII. Field Test Schedule.....largely self-explanatory, but care should be taken to refer to Section II regarding length of operating day, weather effects, operating week, and the time requirements for cleanup.

A.2 PLANNING THE SAMPLING PROGRAM

The background data gathering and the presurvey visit provide the information required on the industry such as process or processes of interest, location of sources of samples whether gaseous, liquid or solid, process conditions that will effect sampling, and safety considerations. The next step is to

plan the sampling program. To do this it is necessary to define clearly the objectives of the program.

A.2.1 Objectives

To establish the objectives of the sampling program it is necessary to define why the testing is to be done and what specific information is required. For the purpose at hand, it is assumed that a major reason for the sampling and analysis scheme is to determine if the industry represents a serious toxic emission source for which control strategies may be required in the future. This implies that samples must be collected for chemical analysis and often for health effect studies. This objective puts different constraints on the sampling program than if the objective were standard setting or compliance sampling.

The objectives of any sampling program must be clearly defined and understood for a number of reasons. First, the overall purpose of the test must be known so that the methods to be used can be determined. Second, the number and kind of samples required must be identified. Each specific sampling point must be determined and the kind and number of samples to be obtained from each identified. Special conditions of the process that are required for sampling at each point and the time requirement for sampling must be specified. Third, the methods to be used to collect samples and data must be specified and any modification or alterations to these methods must be pointed out. Finally, the methods for sample handling and analysis must be given and any deviation from normal procedures indicated.

Once the objectives of the program are outlined, the equipment and manpower needs can be determined. The information taken at the presurvey can be used, along with the knowledge of the objectives and requirements of the job, to set the requirements for equipment and manpower.

A.2.2 Equipment Requirements

The task of making up an equipment list should be assigned to one of the most experienced sampling personnel. He needs to have a knowledge of the equipment inventory of the sampling organization and must be able to mentally visualize each sampling action. Equipment lists of an entire inventory are quite often made up in advance so that necessary items can be checked as needed for the specific job at hand. The entire job then must be thought through, taking each sample at each location into consideration and checking necessary equipment on the list. At this point, some idea of manpower and manhours needed will already have been formed and the sequence of sampling is being established. Some equipment can be reused at a different location by scheduling the sampling at that location later in the program rather than having two pieces of duplicate equipment in the field. One of the prime considerations is to reduce as much as possible the equipment load, while providing sufficient spares so that equipment that is prone to breakage or malfunction can be quickly replaced without destroying the continuity of the sampling program.

A.2.3 Manpower Requirements

The list of required manpower is obviously dictated by the requirements of the sampling program and the scope of the

job. Amplifying factors, however, may cause a change in actual manpower requirement. For instance, a stack or process duct sampling procedure may require only two men if it is close to the ground, but additional men are required if the site is over one hundred feet above the ground. If liquid samples are to be collected at widely separated locations, this also may add team members. The two man crew could easily escalate to four or more due to physical or logistics problems of the job. Conversely, manpower requirements could be less than the typical due to the reverse of the adverse factors. An example is a situation where one man could operate two simultaneous flow control meter stations by alternating reading times. In any event, each job will have to be evaluated on its own merits or disadvantages, and a great deal of judgment is required.

The educational level of required personnel is based, obviously, on an individual's experience, however, general guidelines provide for an Engineer as crew chief, an Engineer or high level technician as Team Leader, and lower level technicians as team members. This personnel mix is, of course, flexible and can be altered to fit the situation.

A.2.4 Job Scheduling

The job must be scheduled, at least in theory, down to the last detail. This requires contact with everyone involved in the sampling program as well as internal sampling and analytical personnel. The plants under study must be contacted to confirm their state of preparedness and to ensure that a shutdown will not conflict with the program. Officials of the government, when they are involved, must be notified of the program dates. Contractors, such as scaffolding erectors

or port welders, must be arranged for, if necessary, and must be contacted in sufficient time prior to the job to do their work. Internally, analytical departments must be cognizant of impending sample arrival, and travel and living arrangements must be made for the sampling team members.

A.2.5 Pretest Briefing

An effective means of relaying information to the sampling crew is a pretest briefing. This is a meeting of all sampling and analytical personnel involved in the program. During the meeting all personnel are given the objectives and the schedule of the job, and specific job assignments are made. Quite often process data are discussed along with sampling methods, sampling locations, number and kinds of samples, and sample handling procedures. The equipment list is discussed and suggestions of the crew are reviewed. This latter point, the suggestions of the crew, is an important step and can serve two purposes. First, it can remind the job organizer of any forgotten items. Second, it promotes understanding of the objectives of the program by the crew. Finally, the pretest briefing brings all personnel together so that essential information can be exchanged. For instance, both analytical and sampling personnel become more familiar with what the organizer requires, analytical personnel become more acquainted with the scope of the program and the required analysis load, and sampling personnel become aware of special problems in areas such as process requirements and sample handling.

After the field portion of the project is completed, it is often beneficial to have a post-test debriefing with the same personnel to discuss problems that occurred. This meeting

is especially beneficial when, during the course of the job, the objectives were altered or for some reason certain samples could not be obtained.

A.2.6 Equipment Checkout

A thorough equipment checkout should be made just before the crew leaves for the job. During the check, each piece of equipment should be tested for functionality and calibrated if required. This procedure should be followed unless a program of check, repair, and calibration on all equipment returned from each job has been established. If this latter procedure is used, all equipment in the storage area will have been checked prior to storage.

A.2.7 Logistics

One person, usually the crew chief, should be made responsible for logistics. In this capacity, he will be in complete control of the movement of all supplies, equipment, and personnel to and from the job site. His responsibility is to see that all materials that need to be packed and shipped will arrive at the job site at the proper time. He makes sure that the proper equipment to do the job is transported to or acquired at the job site in time for use according to the schedule. He is also responsible for the movement of field personnel to the job site. When the job is completed, he becomes responsible for moving supplies, samples, equipment, and personnel to the next job location.

PRELIMINARY SURVEY DATA SHEETS

I. Name of Company _____ Date of Survey _____

Address _____ Phone _____

Name of Contacts _____

EPA Personnel _____ Phone _____

Purpose of Test _____

Pollutants to be Measured _____

Process Type _____

Portion of Process to be Sampled _____

Description of Control Equipment _____

II. Process Description _____

Raw Materials _____

Fuel Burned _____

Products _____

Operations Performed _____

Operating Cycle

Check: Batch _____ Continuous _____ Cyclic _____

Timing of Batch or Cycle _____

Best time to test _____

Abnormal Conditions Affecting Testing

Weather _____

Shutdowns _____

Length of Operating Day _____

Length of Operating Week _____

Other _____

III. Sampling Site

A. Site Description _____

1. Stack

Shape _____

Diameter _____ inches Rectangular _____ x _____

Equiv. Diameters _____

Stack length _____ ft _____ Diameters

Distance before ports _____ ft _____ Diameters

Device _____

Distance after ports _____ ft _____ Diameters

Device _____

Wall Thickness _____ inches

Material _____

2. Ports

Already Installed _____ Size _____

Obstructions _____

Distance to Platforms _____

Supports Required _____

Working Environment _____ Ambient Temp _____ °F

3. Stack Conditions

No. of Traverse Points _____ Stack Temp _____ °C

Stack Velocity _____ Stack Temp _____ °F

Static Pressure _____ inches of water

Moisture Content _____ %

Materials Present _____

Hazards _____

Modifications: Extensions _____

Straightening Vanes _____

Scaffolding _____

Platforms _____

Other _____

4. Access to Site

Height above ground _____ ft Distance to Van _____ ft

Stairs? _____ Elevators? _____ Ladder? _____

Problems _____

B. Methods to be Employed (circle appropriate method)

EPA 1 2 3 4 5 6 7 8 9 10 11 12 13A 13B

14 15 Asbestos Be Hg

Other ASTM PTC27 HC Instrumental (specify) _____

Shell

Others not specified _____

C. Raw Materials and Products to be Collected and Frequency

Fuel _____

Input Materials _____

Products _____

ESP Dust _____

Water Samples _____

Other _____

IV. Safety Checklist

A. Personnel Protection Equipment (check if required)

<u>Item</u>	<u>Plant</u>	<u>MRC</u>	<u>Item</u>	<u>Plant</u>	<u>MRC</u>
Safety glasses		✓	Dust masks		
Goggles			Vapor masks		
Side shields			Air purifying		
Face shields			Air supply		
Hard hats		✓	Air packs		
Ear plugs			Chem. res't clothes		
Safety shoes		✓	Heat res't clothes		
Life belt			Chem. res't gloves		
Ladder climbing device			Heat res't gloves		
Ground fault interrupt			First aid		✓
Grounding clamp			Fire extinguisher		✓

B. Test Site

1. Ladders

General condition _____ Rest stops _____

Cage _____ Special belts _____

Comments _____

2. Scaffold-platforms

General condition _____ Guardrails _____

Toeboards _____ Screening _____

Comments _____

3. Smoking restrictions _____

4. Vehicle traffic rules _____

5. Evacuation procedures _____

6. Alarms _____
7. Hospital location _____
Phone _____
8. Emergency numbers _____

V. Plant Entry

A. Plant Requirements

B. MRC Agreement

C. Potential Problems

VI. Sampling Handling

<u>Method</u>	<u>Cleanup Location</u>	<u>Analysis Location</u>	<u>Shipment</u>		<u>Comments*</u>
			<u>Where to</u>	<u>How</u>	

* Comments to include need for special bottles (Weaton, etc.) and other special handling required.

VII. Level of Effort

<u>Cost Item</u>	<u>Estimated Manhours</u>
1. Planning and Administration	
2. Travel	
3. Setup and Cleanup	
4. Field Testing	
5. Laboratory Analysis	
6. Report Preparation	
7/8. Subcontracting	
9. Presurvey	
10. Sub-total Manhours	
11. Cost per Manhour	
12. Cost of Labor (line 10 times line 11)	
13. Other Direct Costs (Itemized)	

14. Total Cost (line 12 plus line 13)	

VIII. Field Test Schedule

Time Day	AM	PM
Sunday		
Monday		
Tuesday		
Wednesday		
Thursday		
Friday		
Saturday		

APPENDIX A

REFERENCES

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APPENDIX B

FUGITIVE SOURCE DIFFUSION MODEL

The most frequently used model to describe the behavior of pollutants emitted from a source point is the Gaussian diffusion model, or Pasquill-Gifford equation. This model can estimate the concentration of a pollutant at a chosen point at a given distance downwind from the source for a given atmospheric stability and pollutant emission rate. A series of calculations using various combinations of atmospheric stabilities, locations, and sampling times will indicate the range of air quality changes expected to occur around a plant for each pollutant.

Open source sampling efforts must utilize the diffusion model in reverse. Normal use is to predict (estimate) concentrations surrounding a point source of known strength. To calculate a non-point (open) source strength, several concentration readings are taken and the source strength is then determined.

For a number of years estimates of concentrations were calculated either from the equations of Sutton¹ with the atmospheric dispersion parameters C_y , C_z , and n , or from the equations of Bosanquet² with the dispersion parameters p and q .

The general form of the equation of Fickian diffusion, allowing for any spatial variations in the eddy diffusivities, is:

$$\frac{\partial x}{\partial t} + u \frac{\partial x}{\partial x} + v \frac{\partial x}{\partial y} + w \frac{\partial x}{\partial z} = \frac{\partial}{\partial x} \left(K_x \frac{\partial x}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial x}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial x}{\partial z} \right) \quad (1)$$

where x is the concentration, K_x , K_y , and K_z are eddy diffusivities in x , y , and z directions, respectively, and u , v , and w are wind components in the x , y , and z directions. Although a concentration distribution is given by the solution of Equation (1) with certain initial and boundary conditions, it is difficult to obtain any meaningful solution directly from Equation (1). The reasons are that the eddy diffusivities change greatly with stability of the atmosphere, and that the boundary conditions vary with meteorological conditions and surface conditions of the ground.

A solution which was more useful than the solution of the Fickian diffusion equation was obtained by Sutton¹ by introducing the statistical theory of turbulent diffusion which had been suggested by Taylor.³ In his dispersion formulas the eddy diffusivities K_x , K_y , and K_z are replaced by the empirical parameters C_x , C_y , C_z , and n . For the two-dimensional case of Equation (1), Bosanquet obtained a meaningful solution. This is called K-theory and a further development of this theory has been carried out by many meteorologists. The latter type of solution is predominant in most particular urban air pollution computer models being developed and used.

Hay and Pasquill⁴ presented experimental evidence that the vertical distribution of spreading particles from an elevated point was related to the standard deviation of the wind elevation angle, σ_E , at the point of release. Cramer⁵ then derived a diffusion equation based on Sutton's equations

incorporating standard deviations of Gaussian distributions: σ_y for the distribution of material in a plume across wind in the horizontal direction, and σ_z for the vertical distribution of material in the plume. These statistics were related to the standard deviation of wind azimuth angle, σ_A , and wind elevation angle, σ_E , calculated from wind measurements made with a bi-directional wind vane (bivane). Values for these diffusion parameters, σ_y and σ_z , based on field diffusion tests were suggested by Cramer, et al.⁹ Hay and Pasquill also presented a method for deriving the spread of pollutants from records of wind fluctuation. Pasquill further proposed a method for estimating diffusion when such detailed wind data were not available. This method expressed the height and angular spread of a diffusing plume in terms of more commonly observed weather parameters. Suggested curves of height and angular spread as a function of distance downwind were given for several "stability" classes. Gifford¹⁰ converted Pasquill's values of angular spread and height into standard deviations of plume concentration distribution, σ_y and σ_z . Pasquill's method, with Gifford's conversion incorporated, is the commonly accepted calculation method in use today.

Advantages of this system are that (1) only two dispersion parameters are required, and (2) results of most diffusion experiments are now being reported in terms of the standard deviations of plume spread.

In the coordinate system considered here the origin is defined at ground level at or beneath the point of emission, with the x-axis extending horizontally in the direction of the mean wind. The y-axis is in the horizontal plane perpendicular to the x-axis, and z-axis extends vertically. The plume travels along or parallel to the x-axis. Figure B-1 illustrates the coordinate system.

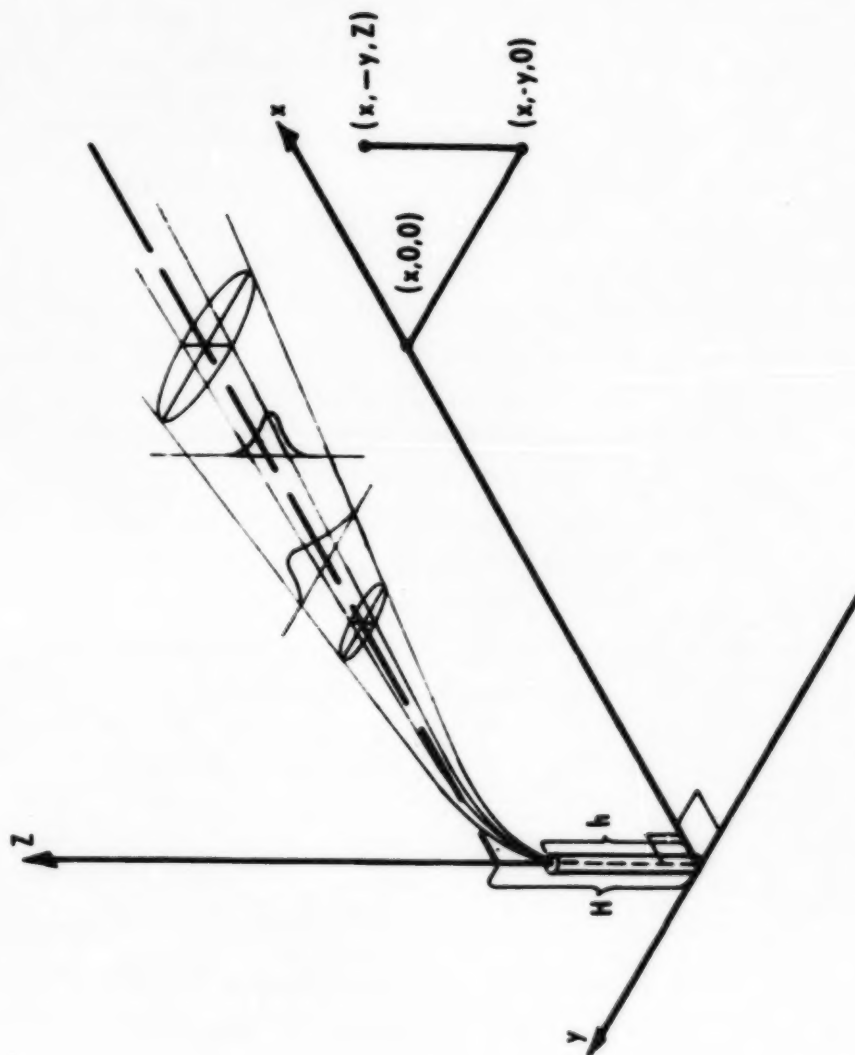


Figure B-1. Coordinate system showing Gaussian distributions in the horizontal and vertical directions.¹¹

The concentration, χ , of gas or particles at point x, y, z from a continuous point source with an effective height, H , is given by Equation (2).

$$\chi(x,y,z;H) = \frac{Q}{2\pi\sigma_y\sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \cdot \cdot \cdot \left\{ \exp \left[-\frac{1}{2} \left(\frac{z-H}{\sigma_z} \right)^2 \right] + \exp \left[-\frac{1}{2} \left(\frac{z+H}{\sigma_z} \right)^2 \right] \right\} \quad (2)$$

The notation used to depict the concentration is $\chi(x,y,z;H)$. H is the height of the plume centerline when it becomes essentially level, and is the sum of the physical stack height h and the plume rise ΔH . The following assumptions are made: the plume spread has a Gaussian distribution in both the horizontal and vertical planes, with standard deviations of plume concentration distribution in the horizontal and vertical of σ_y and σ_z , respectively; the mean wind speed affecting the plume is u ; the uniform emission rate of pollutants is Q ; and total reflection of the plume takes place at the earth's surface, i.e., there is no deposition or reaction at the surface. Any consistent set of units may be used. The most common is χ in g/m^3 , Q in g/sec , u in m/sec , and σ_y , σ_z , H , x , y , and z in meters. The concentration χ is a mean over the same time interval as the time interval for which the σ 's and u are representative. The values of both σ_y and σ_z are evaluated in terms of the downwind distance x , conventionally by graphical methods. Curves have been fitted to these graphs which give excellent agreement.

For concentrations calculated for a source of ground level with no plume rise ($H=0$), Equation (2) simplifies to:

$$\chi(x,y,z;0) = \frac{Q}{\pi\sigma_y\sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{z}{\sigma_z} \right)^2 \right] \quad (3)$$

Where ground level concentrations ($z=0$) are to be calculated further simplification results:

$$x(x,y,0;0) = \frac{Q}{\pi \sigma_y \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \quad (4)$$

And, when the concentration is to be calculated along the centerline of the plume ($y=0$), the equation reduces to:

$$x(x,0,0;0) = \frac{Q}{\pi \sigma_y \sigma_z u} \quad (5)$$

For sampling open sources (those which are not emitted through a stack or vent), whether it is a single operation or several located in one defineable area, MRC uses a downwind array of samplers to determine source strengths or emission rates. Such an array is shown in Figure B-2. It is felt, and borne out by experience, that this technique will give at least three "good" concentration measurements and allows for minor shifts in wind direction. Ideally, the mean wind direction will lie along the path to samplers S_1 and S_3 , but any shift will be detected by either S_2 or S_4 . Concentration values at sampler S_0 are subtracted from the others to determine the effect of the source on downwind concentrations.

For the arrangement shown in Figure B-2, let the origin be defined at the source and all remaining points in the usual Cartesian coordinate system. Let θ be the angle of the mean wind speed. Then to find the value of any point Y_1 perpendicular to the wind direction centerline, the following computation is made.

$$m_1 = \tan \theta$$

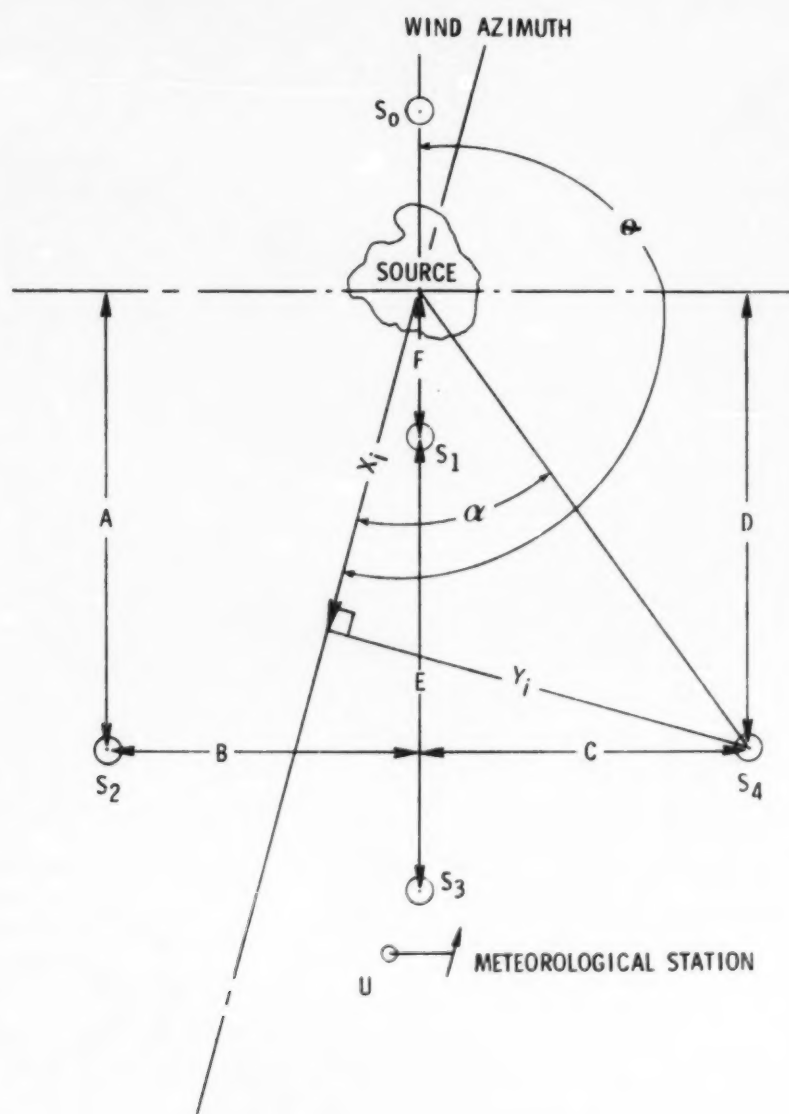


Figure B-2. Sampling arrangement

For point S_1 with coordinates (x_1, y_1)

$$m_2 = \frac{y_1}{x_1}$$

The angle α is found from

$$\alpha = \arctan \frac{m_2 - m_1}{1 + m_1 m_2}$$

The lateral distance Y_1 is

$$Y_1 = (\sin \alpha) \sqrt{x_1^2 + y_1^2} \quad (6)$$

and the downwind distance X_1 is

$$X_1 = (\cos \alpha) \sqrt{x_1^2 + y_1^2} \quad (7)$$

With an open source of some magnitude, the use of the continuous point source diffusion equation is often insufficient to describe the emission rate, and other variations on the Gaussian diffusion model must be utilized. If an open source has a large width to it, a line source model may better describe the emission rate.

Concentrations downwind of a continuously emitting infinite line source, when the wind direction is normal to the line, can be expressed by rewriting an equation of Sutton.¹

$$x(x, y, 0; H) = \frac{2Q_L}{\sqrt{2\pi}\sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right] \quad (8)$$

where Q_L is the source strength per unit distance in g/sec-m. Note that the horizontal dispersion parameter σ_y does not appear in this equation, since it is assumed that lateral

dispersion from one segment of the line is compensated by dispersion in the opposite direction from adjacent segments. Also, y does not appear, since concentration at a given x is the same for any value of y .

Concentrations from infinite line sources when the wind is not perpendicular to the line can be approximated. If the angle between wind direction and line source is ϕ , Equation (8) is modified to:

$$x(x,y,0;H) = \frac{2Q_L}{\sin\phi\sqrt{2\pi}\sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right] \quad (9)$$

for $0 \leq \phi \leq 45^\circ$.

In dealing with diffusion of pollutants in an area having a number of sources, there may be too many sources to consider each source individually. An approximation can be made by combining all the emissions in a given area and treating this area as a source having an initial horizontal standard deviation of plume spread, σ_{y0} . A virtual distance x_y can then be found that will give this standard deviation. Values of x_y will vary with stability. Then equations for point sources may be used, determining σ_y as a function of $x + x_y$.

This procedure treats the area source as a cross-wind line source with an initial normal distribution, a fairly good approximation for the distribution across an area source. The initial standard deviation for a square area source can be approximated by $\sigma_y \approx S/4.3$, where S is the length of a side of the area. The vertical dispersion coefficient σ_z is treated in the regular fashion as having originated from the source rather than a virtual point.

The choice of model for source strength calculation depends on several factors. Sampler locations, personal observations and engineering judgment predominate. MRC routinely calculates emission rates by all three models - point, line, and area source - for open sources since the calculation process is computerized. This enables the data to be checked for agreement between samplers, realistic orders of magnitude for the emission rates, and experiential judgments. Meteorological and plant operating conditions may cause an open source to behave in a different mode on different days.

While the procedure described requires considerable computation, it does provide a method for collecting particulate samples for organic analysis with a reasonable field effort. The equipment requirements of five samplers and a meteorology station is practical and a team of several persons sampling for periods up to a week can obtain the required samples.

APPENDIX B

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